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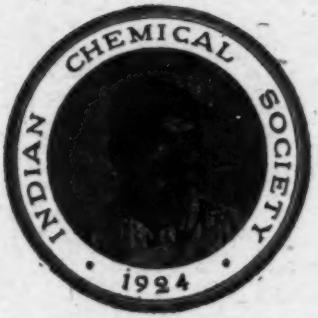

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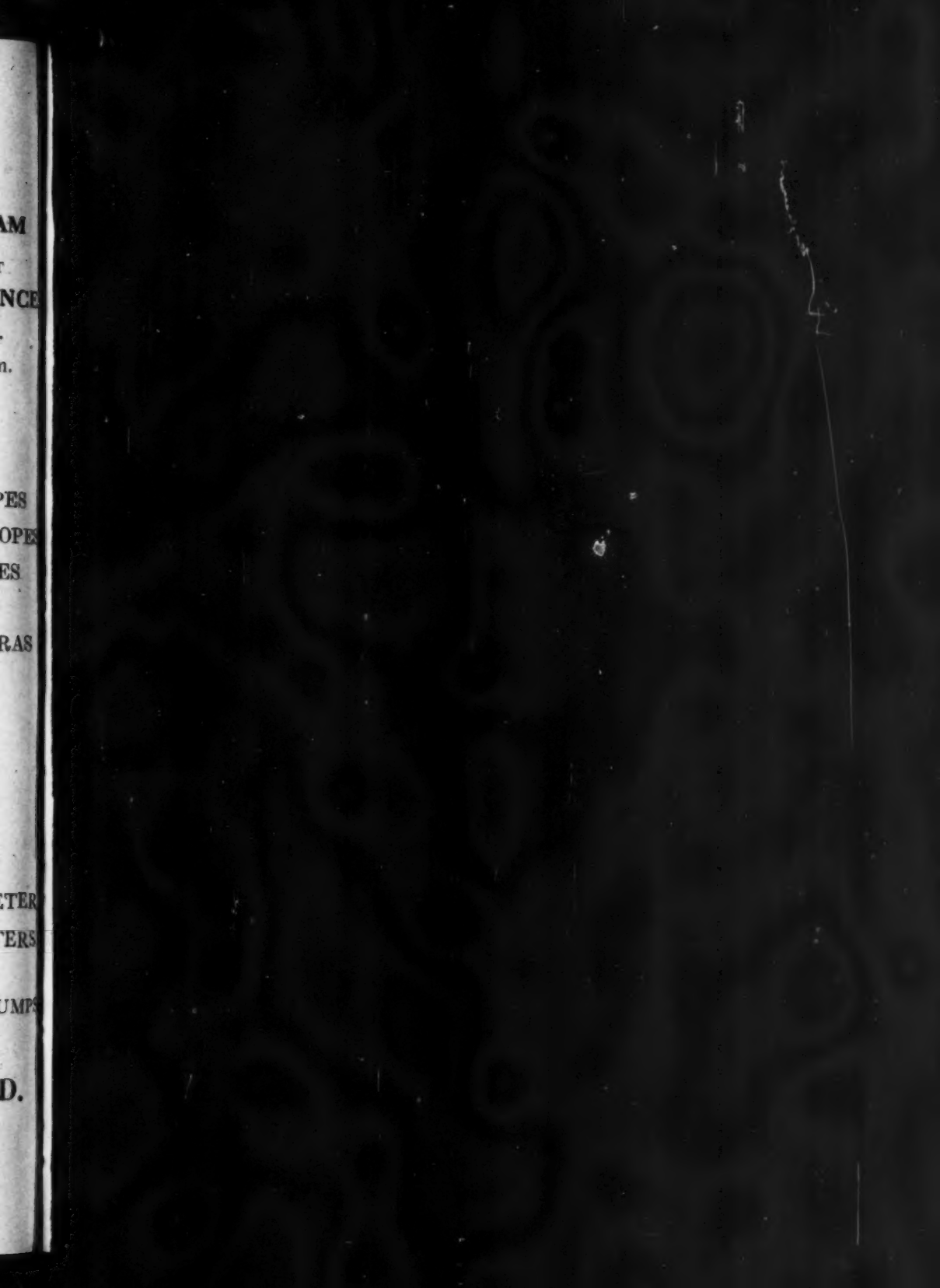

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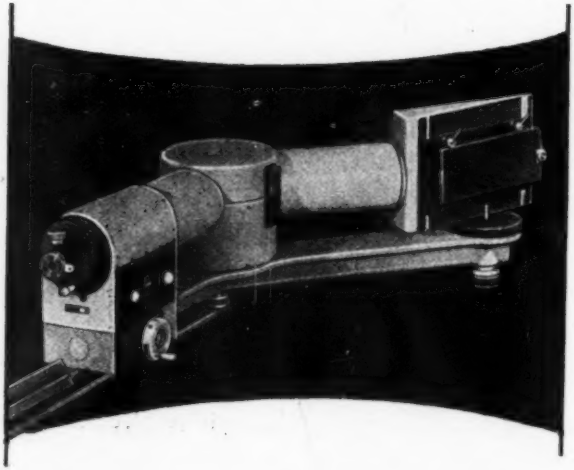

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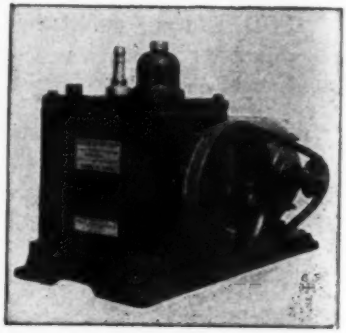

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Studies on the Citrate Complexes of Zinc(II) and Manganese(II)

Rabindra K. Pattnaik and S. Pani

The citrate complex of zinc and manganese have been studied by *p*H titration method and the results corroborated by the measurements of sp. conductance. The reactions taking place may be represented by

$$M^{2+} + H_3Cit \rightleftharpoons C + 2H^+ \quad .. \quad (1)$$
$$C \rightleftharpoons C_1^- + H^+ \quad .. \quad (2)$$
$$C_1^- \rightleftharpoons C_2^{2-} + H^+ \quad .. \quad (3)$$
$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+ \quad .. \quad (4)$$

The equilibrium constants of the reactions (1), (2), (3), and (4) are respectively 6.36×10^{-5}, 4.89×10^{-5}, 2.00×10^{-8}, and 1.35×10^{-5} for zinc citrate and 1.33×10^{-5}, 1.95×10^{-5}, 3.07×10^{-9}, and 2.97×10^{-7} for manganese citrate.

Shin Suzuki (*J. Chem., Soc., Japan, Pure Chem. Sect.*, 1951, **72**, 974) determined the equilibrium constant of zinc citrate complex by potentiometric method with the following ion cell and hydrogen electrode : Hg, HgCl, KCl, KCl, citric acid, $ZnSO_4$, H_2, and found it to be 2.19×10^{-4}.

Korschuhov *et al.* (*Zhur. Neorg. Khim.*, 1957, **2**, 68) have studied the citrate, tartrate, and oxalate complexes of Cd (II) and Zn (II) by the ion exchange method, using the radioactive isotopes. The average values of the instability constants of the compounds, $[Cd(C_2O_4)_2^{2-}]$; $[Cd(C_6H_4O_6)_2^{2-}]$; $[Zn(C_2O_4)_2^{2-}]$; $[Zn(C_6H_4O_6)_2^{2-}]$ and $[Zn(C_6H_5O_7)^{2-}]$ are 2.26×10^{-6}, 3.25×10^{-5}, 7.7×10^{-8}, 2.3×10^{-6} and 2.8×10^{-4} respectively.

EXPERIMENTAL

Three *p*H titrations and two conductivity titrations, performed for the investigation of zinc citrate complex, are recorded in Tables A_1 and A_2 respectively.

TABLE A_1

*p*H *titrations.*

Expt. No.	Temp.	Soln. titrated.	Contents of the soln. titrated.		Soln. and conc. used.	Results.
I	33°	130 c.c.	H_3Cit	0.0030 g. moles	NaOH 0.5 *N*	Fig. 1a, Curve A.
			$NaClO_4$	0.0250		
	33°	130	H_3Cit	0.0030		
			$ZnSO_4$	0.0025	NaOH 0.5*N*	Fig.-1a,
			$NaClO_4$	0.0250		Curve B.
II	33°	100	$NaClO_4$	0.0250	Na_3Cit 0.1*M*	Fig. 2a, Curve A.
	33°	100	$NaClO_4$	0.0250	Na_3Cit 0.1*M*	Fig-2a,
			$ZnSO_4$	0.00125		Curve B.
III°	33°±0.5°	120	Na_3Cit	0.010	NaOH 0.1*N*	Fig-3a,
			$NaClO_4$	0.025		Curve A.
	33°±0.5°	120	Na_3Cit	0.010		
			$ZnSO_4$	0.001	NaOH 0.1*N*	Fig. 3a,
			$NaClO_4$	0.025		Curve B.

TABLE A_2

Conductometric titrations.

Expt. No.	Temp.	Soln. titrated.	Contents of the soln. titrated.		Soln. and conc. used.	Results.
IV	33°	259 c.c.	H_3Cit	0.00030 g.mole	NaOH 0.1*N*	Fig. 4a, Curve A.
	33°	259	H_3Cit	0.00030	NaOH 0.1*N*	Fig.4 a,
			$ZnSO_4$	0.00025		Curve B.
V	32.5°±0.5°	270	Conductivity water		Na_3Cit 0.1*M*	Fig.5 a, Curve A
	32.5°±0.5°	270	$ZnSO_4$	0.00010	Na_3Cit 0.1M	Fig. 5 a, Curve B

For the investigations of manganese citrate complex, four *p*H titrations and two conductivity titrations were performed. The results are recorded in Tables B_1 and B_2 respectively.

TABLE B_1

*p*H *titrations.*

Expt. No.	Temp.	Soln. titrated.	Contents of the soln. titrated.		Soln. and conc. used.	Results.
I	33°	105 c.c.	H_3Cit	0.003 g.mole	NaOH 0.2*N*	Fig 1 b, Curve A.
			$NaClO_4$	0.025		
	33°	105	H_3Cit	0.003		
			$NaClO_4$	0.025	NaOH 0.2*N*	Fig. 1 b,
			$MnSO_4$	0.0025		Curve B
II	33°	85	H_3Cit	0.005		
			$NaClO_4$	0.025	NaOH 0.95*N*	Fig. 2b, Curve A.
	33°	85	H_3Cit	0.005		
			$NaClO_4$	0.025		
			$MnSO_4$	0.0005	NaOH 0.95*N*	Fig. 2b, Curve B
III.	33°±0.5°	100	$NaClO_4$	0.025	Na_3Cit 0.1*M*	Fig. 3b, Curve A.
	33°±0.5°	100	$MnSO_4$	0.00125	Na_3Cit 0.1*M*	Fig. 3b,
			$NaClO_4$	0.025		Curve B.
IV	33°	60	$NaClO_4$	0.010		
			Na_3Cit	0.005	NaOH 0.1*N*	Fig. 4 b, Curve A.
	33°	60	Na_3Cit	0.005	NaOH 0.1*N*	
			$NaClO_4$	0.010		Fig. 4b,
			$MnSO_4$	0.0005		Curve B.

TABLE B_2

Conductometric titrations.

Expt. No.	Temp.	Soln. titrated.	Contents of the soln. titrated.		Soln. and conc. used.		Results.
V	33°	208 c.c.	H_3Cit	0.00033 g.mole	NaOH	0.1*N*	Fig. 5b, Curve A.
	33°	208	H_3Cit $MnSO_4$	0.00033 0.00025	NaOH	0.1*N*	Fig. 5b, Curve B.
VI	32°	110	Conductivity water		Na_3Cit	0.1*M*	Fig. 6b, Curve A.
	32°	110	$MnSO_4$	0.0005	Na_3Cit	0.1*M*	Fig. 6b, Curve B.

DISCUSSION

As found in the study of nickel citrate and other systems, discussed before, the *p*H of the system (B) in each case is lower than the corresponding *p*H in the system (A). Acid is therefore liberated due to the complex formation between the metal ion and citric acid in experiment (I). In case of Zn, the horizontal distance between the two curves at first increases and then decreases. The two curves, however, do not converge and come very close to each other near about the neutralisation point. The two curves are found to diverge above *p*H 7, indicating further liberation of acid in the higher *p*H range.

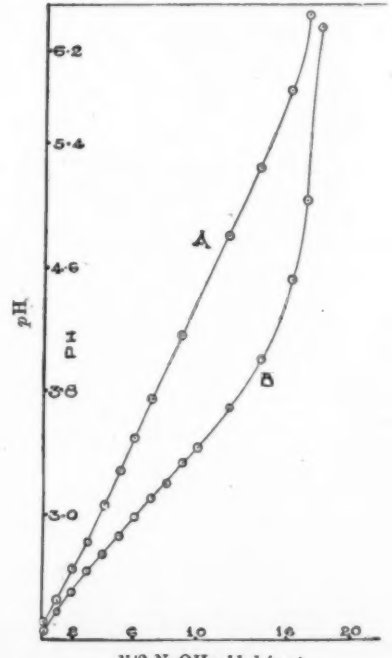
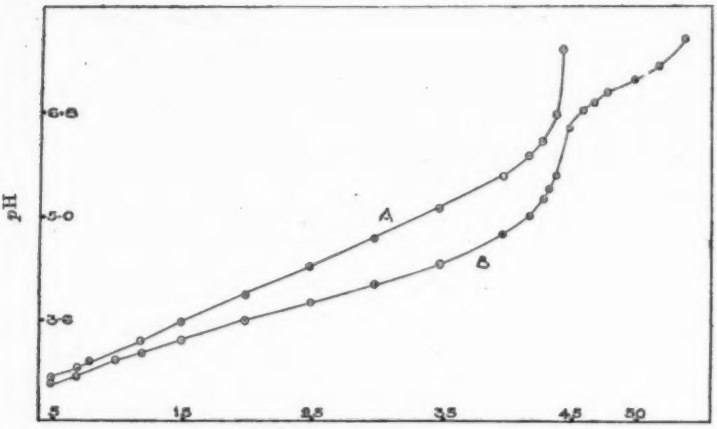
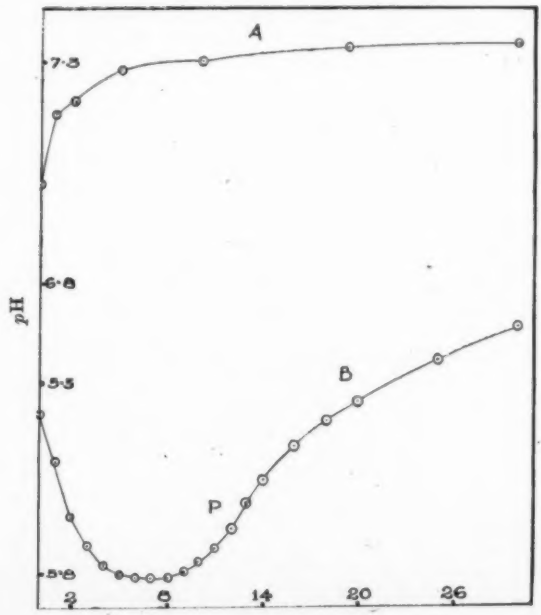


FIG. 1a



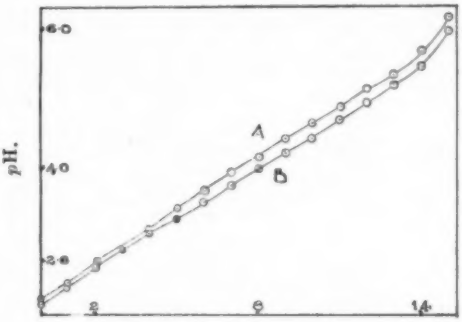
N/5-NaOH *added* (*c.c.*).
FIG. 1b

In case of manganese also the horizontal distance increases to *p*H 5.2 and then decreases to *p*H 6.6. At *p*H 6.6 the horizontal distance between the two curves is very small, but the two curves diverge in the higher *p*H region, indicating liberation of a proton probably from co-ordinated water molecule or hydroxyl group. No proton, however, appears to have been liberated below *p*H 6.6 from the hydroxyl group of citrate ligand due to complex formation, since citric acid would have behaved as a tetrabasic acid in such a case. In



M/10-Na *citrate added* (*c.c.*).
FIG. 2a

experiment II (manganese) the amount of acid liberated is very nearly the same as that obtained in experiment I (Mn). This indicates the formation of a complex containing one citrate ligand per atom of manganese. Formation of a complex containing more than one ligand per atom of manganese even in the system containing metal to citrate in the ratio 1:10 is not indicated.



0.95 *N*-NaOH *added* (*c.c.*).
FIG 2b

Calculation of the Equilibrium Constant

The reaction taking place in expt. (I) in the lower *p*H range is assumed to be similar to that in the cadmium citrate system (Pattnaik and Pani, this *Journal*, 1957, **24**, 673) and may be represented by equation (1) and the equilibrium constant by equation (1-1).

$$M^{2+} + H_3Cit \rightleftharpoons C + nH^+ \qquad (1)$$

(where M = Mn or Zn)

$$\frac{[C]\,[H^+]^n}{[M^{2+}] \times [H_3Cit]} = K \qquad (1\text{-}1)$$

By proceeding in the manner as described in the cadmium citrate system (Pattnaik and Pani, *loc. cit.*) it can be shown that

$$\frac{\triangle[NaOH] \;\; \frac{a}{b} \cdot \triangle[Ct]}{[C]} = n - \frac{a}{b}$$

and when the formation of the complex is complete

$$\frac{\triangle[NaOH] \;\; \frac{a}{b} \cdot \triangle[Ct]}{[MSO_4]} = n - \frac{a}{b}$$

$\triangle$[NaOH], $\triangle$[Ct], [$ZnSO_4$], [$MnSO_4$], a, and b were calculated as before.

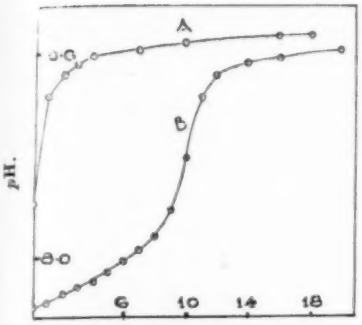
Substituting these values, a series of values of n are calculated for zinc and manganese complexes and collected in Table IA and Table IB. In case of zinc, the value of n is less than 2 below *p*H 3.4 and increases to about 2.8 at *p*H 5.2.

TABLE IA

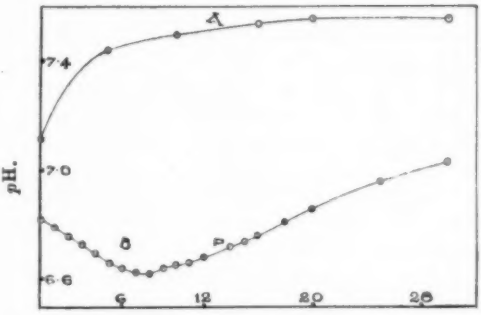
*p*H.	Δ [NaOH]×10².	- Δ [Cit]×10⁴.	*a/b*.	[ZnSO₄]×10².	*n*.	[C] ×10³.	[H₃Cit] ×10².	[Zn²⁺] ×10².	*K*× 10⁵.
2.5	0.2625	1.1	0.2131	1.893	0.3529	1.482	1.6780	1.745	5.059
2.6	0.372	1.5	0.2560	1.882	0.4557	2.156	1.5300	1.667	5.335
2.7	0.515	2.4	0.3046	1.889	0.5839	3.079	1.3580	1.561	5.780
2.8	0.582	2.7	0.3588	1.859	0.3768	3.361	1.2310	1.523	4.502
2.9	0.720	3.3	0.4184	1.848	0.8157	4.611	1.0420	1.384	5.098
3.0	0.856	3.9	0.4822	1.835	0.9584	5.761	0.8720	1.259	5.216
3.1	1.024	4.7	0.5499	1.824	1.1252	7.235	0.6981	1.101	5.939
3.2	1.119	5.2	0.6197	1.812	1.2548	8.341	0.5581	0.978	6.989
3.3	1.283	6.0	0.6911	1.801	1.4263	10.12	0.4111	0.789	7.834
3.7	1.802	8.5	0.9797	1.758	2.0520				
3.8	1.822	8.5	1.052	1.750	2.1560				
3.9	1.842	8.5	1.127	1.744	2.2380				
4.0	1.861	8.6	1.204	1.736	2.3320				
4.1	1.849	8.5	1.282	1.732	2.3890				
4.2	1.804	8.2	1.362	1.726	2.4710				
4.3	1.763	8.2	1.445	1.722	2.5370				
4.4	1.778	8.0	1.530	1.717	2.9550				
4.5	1.709	7.9	1.615	1.712	2.6890				
4.8	1.467	6.8	1.876	1.703	2.8110				
5.0	1.237	5.7	2.049	1.700	2.8446				
5.2	0.984	4.5	2.213	1.699	2.7980				

TABLE IB

*p*H.	Δ [NaOH]×10³.	- Δ [Cit]×10⁴.	[MnSO₄].	*a/b*.	*n*.	[C] ×10³.	[Mn²⁺] ×10².	[H₃Cit] ×10².	*K*× 10⁵.
2.5	1.853	2.7	0.02281	0.2131	0.2968	1.069	2.174	2.078	2.367
2.6	2.07	2.9	0.02252	0.2560	0.3512	1.229	2.129	1.932	1.887
2.7	2.15	4.0	0.02219	0.3046	0.4070	1.340	2.085	1.774	1.442
2.8	2.79	4.1	0.02193	0.3588	0.4928	1.789	2.014	1.954	1.401
2.9	2.89	4.1	0.02166	0.4184	0.5598	1.935	1.973	1.431	1.086
3.0	2.74	4.1	0.02144	0.4822	0.6192	1.935	1.950	1.275	0.7785
3.1	3.68	5.3	0.02114	0.5499	0.7381	2.739	1.840	1.078	0.8712
3.2	4.49	6.4	0.02083	0.6197	0.8542	3.538	1.729	0.8932	0.9120
3.3	4.98	7.1	0.02059	0.6911	0.9568	4.184	1.641	0.7345	0.8714
3.4	5.59	8.0	0.02032	0.7632	1.0684	5.013	1.531	0.5866	0.8844
3.5	6.32	9.1	0.02006	0.8351	1.1880	6.077	1.399	0.4531	0.9583
3.6	6.86	9.8	0.01981	0.9078	1.2990	7.096	1.272	0.3437	1.0240
3.7	7.92	11.3	0.01952	0.9797	1.4423	8.841	1.068	0.2416	1.3640
3.8	8.65	12.3	0.01923	1.052	1.5691	10.490	0.874	0.1651	1.8260
3.9	9.20	13.1	0.01897	1.127	1.6894	12.220	0.675	0.1075	2.6680
4.0	9.49	13.5	0.01871	1.204	1.7977	13.960	0.475	0.0654	4.4300
4.3	10.70	15.4	0.01803	1.445	2.1619				
4.4	10.70	16.0	0.01785	1.530	2.2658				
4.5	10.86	15.6	0.01770	1.615	2.3808				
4.8	9.92	14.2	0.01734	1.876	2.6016				
5.0	9.43	13.6	0.01712	2.049	2.7629				
5.2	7.98	11.4	0.01698	2.213	2.8313				



N/10-NaOH *added* (*c.c.*).
FIG. 3a



0.1*M*-Na *citrate added* (*c.c.*).
FIG. 3b

In the case of manganese, the value of n is less than 2 below *p*H 4.1 and increases with increasing *p*H but less than 3 below *p*H 5.2.

TABLE IIA

*p*H.	$[C_1^-]/[ZnSO_4]$.	$[C]/[ZnSO_4]$.	$K_1 \times 10^5$.
3.7	0.052	0.948	1.095
3.8	0.156	0.844	2.929
3.9	0.238	0.762	3.931
4.0	0.332	0.668	4.969
4.1	0.389	0.611	5.058
4.2	0.471	0.529	5.616
4.3	0.537	0.463	5.813
4.4	0.655	0.345	7.558
4.5	0.689	0.311	7.004
4.8	0.811	0.189	6.800
5.0	0.8446	0.155	5.449
5.2	0.798	0.202	2.492

TABLE II B

*p*H.	$n-2$.	$3-n$	$K_1 \times 10^5$
4.3	0.1619	0.8381	0.968
4.4	0.2658	0.7342	1.441
4.5	0.3808	0.6192	1.942
4.8	0.6016	0.3984	2.393
5.0	0.7629	0.2371	3.218
5.2	0.8313	0.1687	3.110

At lower *p*H the complex is formed with the liberation of two protons due to the reaction of Zn^{2+} or Mn^{2+} and citric acid. Hence the complex is a neutral one. This subsequently ionises like an acid. The reaction may be represented by equation (2) and the equilibrium constant by equation (2-1).

$$C \rightleftharpoons C_1^- + H^+ \qquad .. \qquad .. \qquad (2)$$

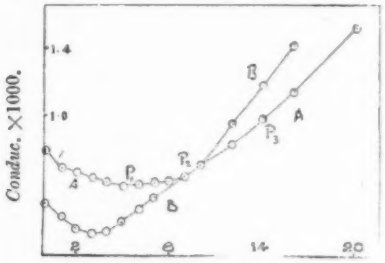
$$\frac{[C_1^-]\,[H^+]}{[C]} = K_1 \qquad .. \qquad .. \qquad (2\text{-}1)$$

It can be shown as before that

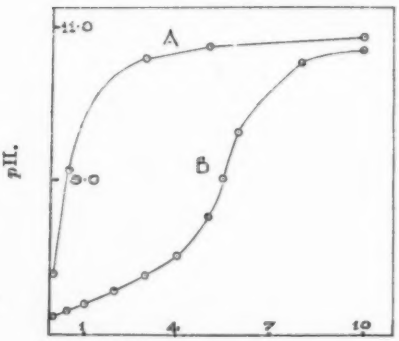
$$\frac{(n-2)\,[H^+]}{(3-n)} = K_1 \qquad .. \qquad .. \qquad (2\text{-}2)$$

[C], [H_3Cit], [Zn^{2+}] and [Mn^{2+}], are calculated as before. The values of equilibrium constant K, obtained by using these values, are shown in Tables IA and IB respectively for zinc and manganese. The mean values of K are 6.36×10^{-5} and 1.33×10^{-5} for Zn and Mn respectively. The values of C and C_1^- and the equilibrium constant K_1 are calculated as before by equation (2-2) and tabulated in Table IIA and Table IIB for Zn and Mn respectively. The mean value of K_1 are 4.89×10^{-5} and 1.93×10^{-5} for Zn and Mn respectively.

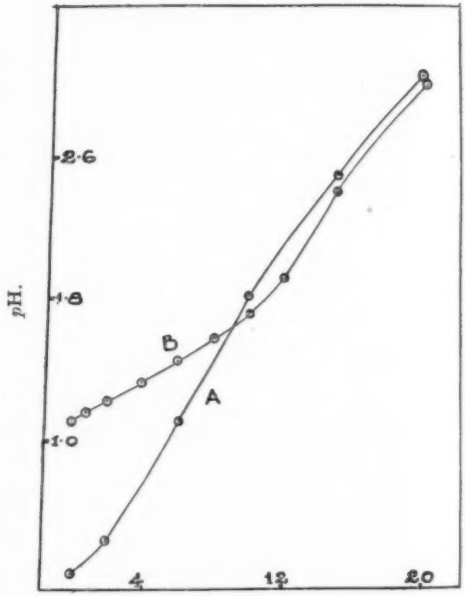
In expt. II of Zn and expt. III of Mn, the curve B is exactly similar to that obtained with the cobalt citrate system in an exactly similar experiment. The *p*H of the system containing no metal ion (Curve A) rapidly rises at the beginning and then rises very slowly with the increasing concentration of sodium citrate. In the system containing metal ion (Zn or Mn) (Curve B) the *p*H falls rapidly at the beginning and then remains very nearly constant for some time. The *p*H increases afterwards rapidly with increasing amount of sodium citrate till the point P is reached. After the point, the rise in *p*H is comparatively slow.



N/10-NaOH *added* (*c.c.*).
FIG. 4a



0.1*N*-NaOH *added* (*c.c.*).
FIG. 4b



0.1*M*-Na *citrate added* (*c.c.*).
FIG. 5a

The reaction of Zn^{2+} or Mn^{2+} ion with citrate ligands results in the formation of a complex and liberation of a proton. The reaction would therefore be similar to that represented in the cobalt citrate system. (Pattnaik and Pani, this *Journal*, 1961, **38**, 364). Hence

$$M^{2+} + Cit^{3-} \rightleftharpoons C_2^{2-} + H^+ \qquad (3)$$

(where M = Zn or Mn)

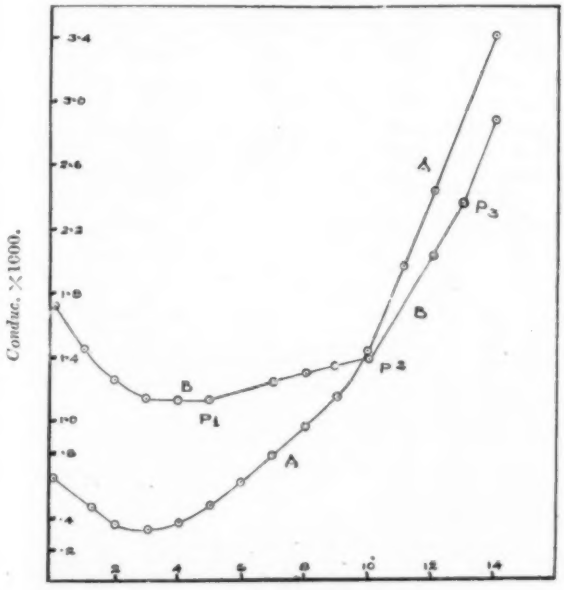
$$\frac{[C_2^{2-}][H^+]}{[M^{2+}][Cit^{3-}]} = K_1 \qquad (3\text{-}1)$$

The reaction alone cannot explain the results since the *p*H does not fall continuously till the formation of the complex is complete. Another reaction is expected to exist which would remove at least some of the protons liberated by the above reaction. Since very little free citrate ions would exist in the solution, removal of protons by citrate ions to any appreciable extent is not expected. The protons are therefore removed by the complex C_2^{2-} by reaction (4).

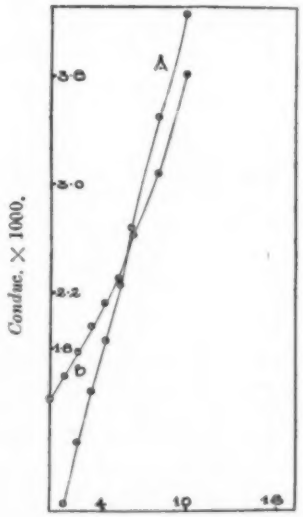
$$C_2^{2-} + H^+ \rightleftharpoons C_1^- \qquad .. \qquad .. \qquad (4)$$

$$\frac{[C_2^{2-}]\,[H^+]}{[C_1^-]} = K_2 \qquad .. \qquad .. \qquad (4\text{-}1)$$

The complex C_2^{2-} would exist only in the higher *p*H range and when the *p*H is lowered, it is converted to C_1^- by the above reaction.



0.1 *N*-NaOH *added (c.c.).*
FIG. 5b



0.1 *M*-Na *citrate added (c.c.).*
FIG. 6b

At the beginning, more of C_2^{2-} is formed and hence the *p*H falls rapidly. When the *p*H is sufficiently lowered, the complex C_2^{2-} is no longer formed, but the complex C_1^- is formed by reaction (4) or (5). This would produce the same result.

$$M^{2+} + Cit^{3-} \rightleftharpoons C_1^- \qquad .. \qquad .. \qquad (5)$$

The concentration of C_2^{2-} does not increase and there is no liberation of acid due to formation of C_1^-; as such the *p*H remains very nearly constant for some time. After this the *p*H rises comparatively rapidly due to increasing concentration of free citrate ion in the solution. As the *p*H is increased, reaction (4) moves in the reverse direction. There is a break in curve B at point P. This comes when a little more than one g. mole of sodium citrate per g. atom of metal concerned is added. This break most probably in-

dicates complete formation of the 1:1 zinc citrate and manganese citrate complexes. Above the inflection point, the reaction taking place is the dissociation of the complex C_1^- to H^+ and C_2^{2-}.

K_2 was determined as before above the inflection point as calculated in the cobalt citrate system (Pattnaik and Pani, *loc. cit.*). The values are shown in Table IIIA and IIIB. The mean values of K_2 are 2.000×10^{-8} and 3.07×10^{-9} for Zn and Mn respectively.

TABLE IIIA

*p*H.	[$ZnSO_4$].	[Ct].	Z.	[$HCit^{2-}$]$\times10^4$.	[C_2^{2-}]$\times10^4$.	[C_1^-].	$K_2\times10^8$.
6.25	0.01086	0.01304	6.7750	3.218	3.303	0.01053	1.765
6.30	0.01077	0.01379	7.4773	4.041	4.138	0.01036	2.002
6.35	0.01069	0.01453	8.2629	4.646	4.749	0.01022	2.075
6.40	0.01055	0.01553	9.1467	5.445	5.547	0.01000	2.209
6.45	0.01039	0.01694	10.1397	6.460	6.569	0.00974	2.393
6.50	0.01023	0.01817	11.2477	7.063	7.167	0.00952	2.381
6.55	0.01008	0.01936	12.4969	7.429	7.532	0.00933	2.275
6.60	0.00990	0.02076	13.9061	7.821	7.905	0.00911	2.179
6.65	0.00972	0.02224	15.4755	8.093	8.183	0.00890	2.058
6.70	0.00950	0.02402	17.2449	8.424	8.498	0.00865	1.960
6.80	0.00902	0.02785	21.4439	8.784	8.850	0.00813	1.725

TABLE IIIB

*p*H.	[Ct].	[$MnSO_4$].	Y.	[$HCit^{2-}$]$\times10^4$.	[C_2^{2-}]$\times10^4$.	[C_1^-].	$K_2\times10^9$.
6.75	0.01335	0.01137	19.2243	1.930	1.942	0.01126	1.646
6.80	0.01481	0.01118	21.4438	1.693	1.708	0.01101	2.458
6.85	0.01639	0.01097	23.9434	2.264	2.810	0.01074	3.000
6.90	0.01803	0.01076	26.7331	2.719	2.737	0.01049	3.285
6.95	0.01948	0.01057	29.8727	2.984	2.998	0.01027	3.275
7.00	0.02138	0.01031	33.4024	3.313	3.331	0.00998	3.337

Below the inflection point Zn and Mn exist partly as Zn^{2+} and Mn^{2+} and partly as complexes. Hence

$$[MSO_4] = [M^{2+}] + [C_1^-] + [C_2^{2-}].$$

K_4 was calculated as before (as determined in cobalt citrate system). The values are collected in Tables IVA and IVB.

TABLE IVA

*p*H.	[Ct]$\times10^3$.	[$ZnSO_4$] $\times10^2$.	r.	p.	q.	[$HCit^{2-}$] $\times10^5$.	[C_2^{2-}] $\times10^5$.	[C_1^-] $\times10^3$.	[Zn^{2+}] $\times10^2$.	[Cit^{3-}] $\times10^4$.	$K_4\times10^5$.
5.89	5.561	1.180	1.0633	3.5466	62.20	8.011	8.643	5.290	0.643	2.05	8.447
5.90	4.762	1.191	1.0618	3.6039	60.81	6.889	7.444	4.450	0.739	1.70	7.461
5.95	3.474	1.206	1.0551	3.9145	54.31	5.578	5.996	3.196	0.881	1.64	7.656
6.00	2.534	1.218	1.0914	4.2645	48.51	4.504	4.825	2.292	0.984	1.49	3.291
6.05	2.056	1.224	1.0438	4.6579	43.35	4.039	4.306	1.824	1.038	1.49	2.481
6.10	1.671	1.229	1.0390	5.0985	38.74	3.619	3.839	1.449	1.081	1.48	1.905
6.15	1.380	1.233	1.0348	5.5934	34.63	3.273	3.457	1.162	1.114	1.52	1.445
6.20	1.186	1.235	1.0310	6.1505	30.97	3.064	3.222	0.966	1.136	1.58	1.132
6.25	0.990	1.238	1.0276	6.7748	27.72	2.768	2.899	0.775	1.158	1.60	0.882
6.30	0.5965	1.243	1.0246	7.4773	24.81	1.777	1.870	0.445	1.197	1.16	0.676

The mean value of K_4 are 3.85×10^{-5} and 2.89×10^{-6} for Zn and Mn respectively.

TABLE IVB

pH.	[Ct]$\times 10^3$.	[$MnSO_4$]	P.	q.	r.	[$HCit^{2-}$] $\times 10^5$.	[C_2^{2-}] $\times 10^5$.	[C_1^-] $\times 10^3$.	[Mn^{2+}] $\times 10^3$.	[Cit^{3-}] $\times 10^4$.	$K_4 \times 10^6$.
6.70	3.661	0.01265	17.2449	65.98	1.0098	4.350	4.413	2.867	9.74	7.07	1.278
6.65	5.124	0.01246	15.4755	73.91	1.0110	5.663	5.749	4.192	8.21	8.19	1.914
6.62	6.542	0.01227	14.5159	79.12	1.0117	6.896	7.003	5.471	6.73	9.33	2.675
6.65	9.419	0.01189	15.4755	73.91	1.0110	10.420	10.560	7.698	4.08	15.12	3.831
6.70	11.340	0.01163	17.2449	65.98	1.0098	13.510	13.670	8.882	2.61	21.90	4.772

Now it can be shown that

$$\frac{K_4 \times k_1\, k_2\, k_3}{K_1 \times K_2} = \frac{[C]\,[H^+]^2}{[M^{2+}]\,[H_3Cit]} = K$$

By substituting the values of K, K_1, K_2, K_4, k_1, k_2, and k_3, it is found that the values of

$$\frac{K_4 \times k_1\, k_2\, k_3}{K_1 \times K_2}$$

are equal to 0.366×10^{-5} and 0.5348×10^{-5} for Zn and Mn respectively, whereas the value of K (obtained before in the expt. I) is 5.73×10^{-5} for zinc and 1.331×10^{-5} for manganese. Hence both the values are not equal as seen in the case of cobalt, discussed before. The low value of

$$\frac{K_4 \times k_1\, k_2\, k_3}{K_1 \times K_2}$$

may be due to the low value of K_4, which might have been due to the hydrolysis of Zn^{2+} ion to $ZnOH^+$ ion and Mn^{2+} to $MnOH^+$ according to equation (6). This type of hydrolysis may occur to an appreciable extent at higher pH. The K_4 is determined above pH 5.9 in case of Zn and above 6.6 in case of Mn, but K is determined at pH below 3.4 in both cases.

$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+ \qquad \ldots\ldots\ldots\ldots \quad (6)$$

The hydrolysis constant of this reaction may be represented by equation (6-1).

$$K_h = \frac{[MOH^+]\,[H^+]}{[M^{2+}]} \qquad \ldots\ldots \quad (6\text{-}1)$$

Calculation of Hydrolysis Constant

Since Zn^{2+} and Mn^{2+} ions are partly hydrolysed, the free zinc and free manganese assumed to be present as Zn^{2+} or Mn^{2+}, calculated for the determination of K_4, are not correct. Therefore the concentration of Zn^{2+} and Mn^{2+} would be less. The value of K_4 would therefore be more. It is assumed that the hydrolysis of Zn^{2+} and Mn^{2+} below pH 3.4 is negligible.

The hydrolysis constant was calculated in a manner similar to that adopted for the calculation of the hydrolysis constant of the cobalt ion (*loc. cit.*). The values are given in Tables VA and VB for Zn and Mn respectively. The mean values of K_h are 1.35×10^{-5} for Zn and 2.97×10^{-7} for Mn.

Further, it is mentioned in the International Critical Table (Vol. 7,p. 252) that hydrolysis of Zn^{2+} to $ZnOH^{+}$ according to equation (6) is 0.0416% and 0.0244% in aquous solutions of zinc sulphate of concentration 0.0157*M* and 0.0244 *M* respectively.

The hydrolysis constant K_h, if calculated from the above results, would be 2.83×10^{-5} and 3.97×10^{-5} respectively. Hence the results obtained in this experiment agree with the above results of Zn.

TABLE VA

*p*H.	[Zn]$\times 10^2$.	$\frac{K_4k_1k_2k_3}{K \times K_1 K_2}$.	[Zn^{2+}]$\times 10^4$.	[$ZnOH^{+}$].	$K_h \times 10^5$.
5.90	0.739	0.06393	4.724	0.00692	1.844
6.00	0.984	,,	6.291	0.00922	1.465
6.10	1.081	,,	6.910	0.01012	1.163
6.20	1.136	,,	7.263	0.01064	0.924

TABLE VB

*p*H.	[Mn]$\times 10^3$.	$\frac{K_4k_1k_2k_3}{K \times K_1 \times K_2}$.	[Mn^{2+}]$\times 10^3$.	[$MnOH^{+}$]$\times 10^3$.	$K_h \times 10^7$.
6.75	11.38	0.4026	4.582	6.80	2.638
6.70	9.74	,,	3.922	5.82	2.961
6.65	8.21	,,	3.306	4.90	3.319

In expt. III for Zn and expt. IV for Mn the results are very nearly identical to that obtained in similar experiment in the cobalt citrate system. The curve B is similar to the neutralisation curve of an acid. It is of interest to note that the neutralisation point is reached at about 11c.c. of 0.1*N*-NaOH in case of Zn and at 5.5. c.c. of the same alkali in case of manganese.

The *p*H attained by the solution containing Zn by the addition of 11 c.c. of 0.1*N* alkali is reached by the other solution on addition of 1c.c. of the same alkali, *i.e.*, 0.001g. mole of sodium hydroxide is consumed by the complex formed from 0.001 g. mole of zinc sulphate. The *p*H attained by the solution containing Mn by the addition of 5.5. c.c. of *N*/10 alkali is reached by the other solution on adding 0.5 c.c. of the same alkali, *i.e.*, 0.0005 g.moles of NaOH is consumed by the complex formed from 0.0005 g. moles of manganese sulphate. Further liberation of one equivalent of proton indicates the formation of C_2 complex in each case.

In expt. IV of zinc and expt. V of manganese, the nature of the curves A and B are similar to those obtained in the case of cobalt citrate system. A break in curve B, similar to that in curve A at the neutralisation point, comes much later, indicating the former system to contain more acid.

A neutral complex is formed in the beginning which does not contribute to the conductance of the solution. The neutral complex then dissociates like dibasic acid to complexes C_1^- and C_2^{2-}. The formation of these complexes are indicated by breaks at P_1, P_2, and P_3 respectively.

In expt. V of Zn and expt. VI of Mn, the nature of the curves is similar to that obtained in the investigation of the cobalt citrate system. Hence the formation of 1:1 complex is indicated here also

The structure of the zinc citrate and manganese citrate complexes are just similar to that of cadmium citrate complexes (Pattnaik and Pani, *loc. cit.*, p. 673) and nickel citrate complexes (Pattnaik and Pani, this *Journal* 1957, **34**, 619) discussed earlier.

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Studies on the Stability and Electrokinetic Potential of Ceric Oxide Sol

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Positively charged ceric hydroxide sol has been prepared by dialysing a 3% ceric ammonium nitrate solution. The following equation connecting ζ with ζ_a has been found to hold good both for rapid and slow rates of coagulation:

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m.\frac{1}{S}$$

where ζ_a represents apparent zeta-potential calculated from the Smoluchowski equation, S, the specific conductance of the solution of an electrolyte at its equicoagulating concentration, ζ, the true zeta-potential, and m, a constant under the conditions of the experiments.

The electrolytes used for coagulation are: NaCl, Na_2SO_4, K_3FeCy_6, and mixtures of NaCl and Na_2SO_4 and NaCl and K_3FeCy_6.

The values of ζ (true zeta-potential) found from (Fig. 1) are 25.6 mv and 26.7 mv for rapid and slow rates of coagulation respectively.

It has been shown by Ghosh and co-workers (*Trans. Faraday Soc.*, 1953, **49**, 1477; *Science & Culture*, 1954, **18**, 489; this *Journal*, 1954, **31**, 274, 393) that the true zeta-potential, ζ, of colloidal particles in presence of equicoagulating concentrations of electrolytes containing counter ions of different valencies can be found by using the equation,

$$\frac{1}{\zeta_a} = \frac{1}{\zeta} + m.\frac{1}{S} \qquad \ldots \qquad \ldots \qquad (1)$$

where ζ_a represents the apparent potential calculated from electro-osmotic data by the Smoluchowski equation, S is the specific conductance of the solution in equilibrium with the colloidal particles, and m is a constant under the conditions of the experiments. For electro-osmosis

$$m = \frac{3V_1X}{\zeta V_2 R}$$

where V_1 and V_2 represent the volume of the solid and solution respectively in the diaphragm, R is the radius of the colloidal particles, and X, sp. surface conductance.

These authors have also concluded from their results that a given rate of coagulation of a colloid is characterised by a definite value of the true zeta-potential independent of the valency of the counter ions used. With a view to ascertaining the applicability of the theories advanced by those authors, experiments have been undertaken with ceric oxide sol.

EXPERIMENTAL

Preparation of the Colloid.—Positively charged ceric oxide hydrosol was prepared by the dialysis of a solution of ceric ammonium nitrate (Blitz, *Ber.*, 1902, **35**, 4431; *Z. anorg.*

Chem., 1927, **168**, 93). A 3% solution was allowed to stand for five days, when a slightly turbid, greenish yellow sol resulted. This was first electrodialysed for 12 to 15 hours and then dialysed in cellophane bags for about 3 weeks. Its ceric oxide content was 0.5% and the specific conductance was 1.421×10^{-4} mhos at 25°.

Determination of the Equicoagulating Concentration.— A given volume of electrolyte (2 c.c.) was mixed with an equal volume of the sol and the mixture was left as such for 10 minutes or 20 hours for rapid or slow rates of coagulation respectively. The mixture was centrifuged afterwards for 2 minutes at a definite speed and the supernatant solution was examined for transparency or opacity. The concentration of the electrolyte, which just gave a transparent supernatant solution, was taken as the equicoagulating concentration. The electrolytes used for rapid and slow rates of coagulation were: NaCl, Na_2SO_4, K_3FeCy_6, and mixtures of NaCl and Na_2SO_4 and of NaCl and K_3FeCy_6.

Electro-osmotic Experiments

The electro-osmotic experiments were carried out at 25° by Bredig's method in the U-tube apparatus as described by Mukherjee *et al.* (this *Journal*, 1927, **4**, 493). A definite volume of the electrolyte solution was mixed with an equal volume of the colloid so that the final concentration of the electrolyte in the mixture represented its coagulating concentration. The mixture was allowed to stand for 10 minutes or 20 hours according as the rate of coagulation was rapid or slow. The coagula were then separated from the supernatant liquid by centrifuging and were transferred to a U-tube. The U-tube containing the coagula was next centrifuged so that the coagula occupied a definite volume in each of the experiments, thereby securing the constancy of V_1 and V_2 as required by equation (1). R can be assumed constant since the coagulation procedure was closely standardised. Centrifugate was used for the supernatant liquid and its specific conductance was determined.

The velocity of electro-osmotic flow was measured from the rate of movement of the air bubble. The current passing through the diaphragm was noted and the values of ζ_a were calculated from the Smoluchowski equation. The reproducibility of the electro-osmotic data was found to be within ±3%.

The extrapolated values of the true zeta-potential of ceric hydroxide sol in the region of rapid and slow rates of coagulation were found to be 25.6 mv and 26.7 mv.

The values of $1/\zeta_a$ were plotted against the corresponding values of $1/S$ in Fig. 1 in which the straight line (I) represents rapid and the line (II), slow coagulation respectively.

DISCUSSION

In the zone of rapid coagulation the vaues of ζ_a found for different electrolytes vary from 12.4 to 24.8 mv, but they satisfy the linear relationship as required by equation (1).

For slow coagulation the values of ζ_a found for different electrolytes vary from 15.5 to 25.4 mv. The plot of the values of $1/\zeta_a$ against the corresponding value of $1/S$ yields, however, a straight line as required by equation (1).

At the equicoagulating concentrations of the electrolytes and their mixtures, under the conditions of our experiments, ζ and m therefore remain constant. The values of ζ and m, found from the intercept and the slope of the straight line (I) for rapid coagulation, are 25.6 mv and 6.872×10^{-3} respectively.

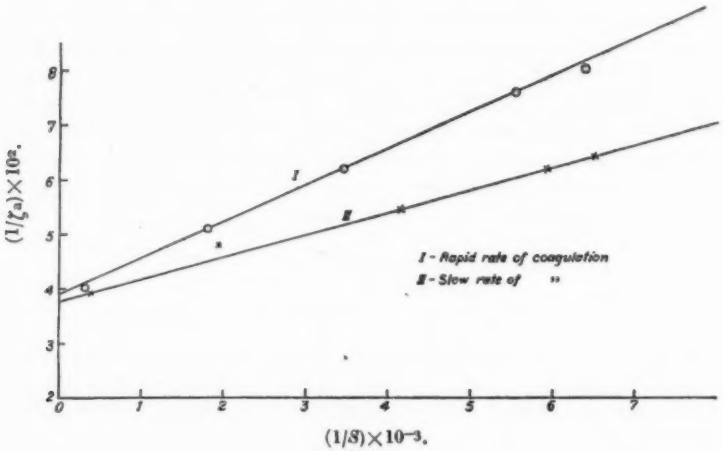

FIG. 1

The experimental results also lead to the conclusion that a given rate of coagulation of the ceric oxide sol by the electrolytes used is characterised by a definite value of true zeta-potential, independent of the valency of the counter ions used.

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Properties of Mixtures of Clay Minerals. Part I. Binary Mixtures

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After estabiishing the purity of clay mineral by a combination of chemical, physical, electrochemical, and viscosity measurements studies have been made of properties of binary mixtures (20 : 80 ; 40 : 60 ; 50 : 50 & 80 : 20) of montmorillonite, kaolinite, and illite. The variations in the characteristics of D. T. A. curves, *p*H, specific conductance, viscosity, and cation activities on the progressive addition of bases to these mixtures have been studied. It has been observed that individual clay mineral components in the mixtures investigated can be detected only by a combination of the methods used.

Clay material, the active inorganic constituent of clay adsorption complex, is composed of a number of secondary aluminosilicate minerals, known as clay minerals. The common clay minerals found in the soil are kaolinite, montmorillonite, and illite. The occurrence of chlorite has also been reported in some soils (Mitra and Rao, *Proc. Nat. Inst. Sci. India*, 1960, **26**, 81). It has been observed that properties of soil are dominated to a large extent by the nature and amount of clay minerals present in them. In view of the importance of the clay-mineral studies in agriculture and engineering and ceramic, petroleum, and other industries, several investigators pursued the work on the identification and estimation of clay minerals present in soils. X-ray, differential thermal analysis, chemical, electrochemical, and viscous methods have been requisitioned for this purpose. Since the soils usually contain a mixture of clay minerals, the first phase of investigation of clay mineralogy consists in the studies of the properties of the prepared mixtures of clay minerals.

Grim and his collaborators (*Am. Mineral*, 1947, **32**, 493; 1942, **27**, 801; "X-ray Identification and Structure of the Clay Minerals", Mineralogical Society of Great Britain Monograph, 1951) and Spiel *et al.* (U. S. Bur. Mines, Tech. paper, 1945, 664), have published differential thermal analysis curves of prepared mixtures of various clay minerals. The main findings of these investigators are that (*i*) in mixtures of discrete particles, the dehydration characteristics reflect those of individual components; (*ii*) in interlayer mixtures, the characteristics of individual components are registered in the D. T. A. data in some cases although in others they are not; (*iii*) thermal characteristics of clay-mineral mixtures depend on the intimacy of mixing and on the nature of clay mineral themselves; (*iv*) sometimes dehydration characteristics of individual components are changed so much that even 25% of a component may be easily masked in presence of the other constituent. Adhikari (*J. Indian Soc. Soil Sci.*, 1958, **6**, 147) has studied the thermal dehydration characteristics of a mixtures of aquagel (montmorillonitic) and oxide-free clay isolated from Kakdwip and also of Rajmahal kaolin (kaolinite) and oxide-free clay from Kakdwip in different proportions. The Kakdwip clay is, however, mostly illitic, but contains some kaolinite (Adhikari, *Indian J. Appl. Chem.*, 1958, **21**, 149). The individual characteristics of the clay minerals have been found to be reflected in the D. T. A. curves.

Chakravarti (*J. Indian Soc. Soil Sci.*, 1954, **2**, 127; 1958, **6**, 239) using binary mixtures of montmorillonite and kaolinite, Roy and Das (*Bull. Nat. Inst. Sci. India*, 1954, **3**, 165) with mixtures of H-bentonite and H-illite, and Adhikari (*loc. cit.*) using the above mentioned mixtures have shown from the *p*H—alkali concentration curves and from viscosity—base-saturation curves of the mixtures that b. e. c.'s of the mixtures are additive.

These investigators apparently paid no adequate consideration to the purity of the clay minerals used and did not study their purity by multiple methods, viz., X-ray, D.T.A., chemical, and electrochemical. This is very important because Grim ("Clay Mineralogy", McGraw Hill, 1953) has clearly mentioned that "Unless the clay mineral analyses are made by a combination of X-ray diffraction, differential thermal, and chemical methods and unless the procedures are detailed, the completeness of the results is questionable". Consequently, the data obtained by these investigators do not appear to be of much value for the purpose of standardising the properties of mixtures of pure clay minerals. This information is essential for the determination of clay minerals in soils because soils usually contain a mixture of these minerals. The first phase of the present study (*Proc. Indian Sci. Cong.*, 1959, Part III, p. 490) was therefore confined to testing the purity of clay minerals used by a combination of methods, viz., X-ray, D.T.A., and chemical analysis and by studying the variations in *p*H, conductance, viscosity, and ion activity with progressive addition of bases to the H-clays prepared from the clay minerals used. Having established the purity of the samples, the next phase of the investigation consisted (*ibid.*, p. 491) in studying the properties of binary mixtures of H-clays prepared from the tested samples of clay minerals. The present communication deals with the details of the experimental procedures and results obtained.

EXPERIMENTAL

Clay fractions ($<2\,\mu$) were separated from a sample of kaolin (Rajmahal), a sample of American bentonite (montmorillonite), and a sample of illite (grundite) by the usual process of dispersion and sedimentation. The separated fractions were treated with H_2O_2 to remove organic matter and subjected to electrodialysis in order to obtain H-clays.

For preparation of mixtures H-clays, prepared from pure clay minerals of different proportions (proportions by weight on oven-dry basis), were mixed in suspension by stirring, kept for 6 months in wet condition in well-stoppered Jena glass bottles for attainment of equilibrium, and then all measurements were made. The following mixtures were studied:

(*a*) Kaolinite and montmorillonite (20 : 80, 40 : 60, 50 : 50, 80 : 20)
(*b*) Kaolinite and illite (20 : 80, 40 : 60, 50 : 50, 80 : 20)
(*c*) Montmorillonite and illite (20 : 80, 40 : 60, 50 : 50, 80 : 20)

Chemical analyses were carried out by fusion with Na_2CO_3 of the hydrogen clays (dried at 105° for 16 hours) following the usual procedure. For X-ray diffraction analysis, H-clays were treated with glycerol in the form of a ternary solution (glycerol, ethanol, and benzene) according to the technique adopted by White and Jackson (*Proc. Soil Sci. Soc. Amer.*, 1946, **2**, 150) and powder diagrams were taken using Philip's sealed tube with Cu-target and adjustable plate camera. Differential thermal analyses (D. T. A.) of H-clays (dried at 105° for 16 hours) were carried out in an apparatus with a heating rate of 10°

per minute. Variations in *p*H, specific conductance, viscosity, and cationic activity of H-clays on the addition of increasing amounts of KOH and $Ca(OH)_2$ were measured. For this purpose increasing amounts of bases were added to 10 c.c. of H-clay suspensions kept in several well-stoppered Jena glass bottles, final clay concentration being adjusted to 0.5% by the addition of requisite amounts of water. The measurements were made after 24 hours. The *p*H was measured with the help of a Cambridge *p*H meter using glass electrode, viscosity with an Ostwald viscometer, conductance with a Leeds-Northrup conductivity bridge, and cation activity with clay-membrane electrodes (Chatterjee., *J. Indian Chem. Soc., Ind. & News Ed.*, 1949, **12,** 73) using the procedure of Marshall *et al.* (*J. Amer. Chem. Soc.*, 1941, **63,** 1911; *Proc. Soil Sci. Soc. Amer.*, 1946, **2,** 171).

X-ray Diffraction Analysis.—The results of X-ray analysis of the glycerol-treated bentonite used show very sharp reflections at 17.73 KX, 9.217 KX and 3.411 KX. Very strong reflexions at 7.316 KX and 3.667 KX were observed in case of the kaolin sample used. The illite sample used gives strong basal spacings at 9.98 KX. The results of X-ray analysis therefore indicate that samples of bentonite, kaolin, and illite are pure montmorillonite, kaolinite, and illite respectively.

Differential Thermal Analysis (*D. T. A.*).—The bentonite used showed an initial endothermic reaction corresponding to the loss of interlayer water at 185 95°, a second endothermic reaction at 700-10° due to loss of OH-lattice water, and a third endothermic peak at 890° where dehydration was complete. It also showed an exothermic peak at 920°. The thermal reaction of the American bentonite showed the characteristics of a montmorillonite. An endothermic peak at 600-10° and one very sharp exothermic peak at 970-80°, characteristic of a well-crystalline kaolinite, were observed in the D.T.A. curve of the kaolin sample used. The illite sample used showed three endothermic peaks at 135°, 580°, and 890° respectively and an exothermic peak at 950-55°, indicating that the sample is a pure illite.

Chemical Analysis.—SiO_2/Al_2O_3 mole ratios of the clay samples of bentonite, kaolin, and illite used are 4.25, 1.96, and 3.06 respectively. Calculation of lattice charge from chemical analysis data according to the procedure adopted by Marshall ("The Colloid Chemistry of the Silicate Minerals", Academic Press, N. Y., 1949), carried out with the samples of bentonite and illite clays, shows both the clays to be of 2:1 lattice type of clay minerals. SiO_2/Al_2O_3 mole ratio of the kaolin clay indicates that its lattice is of 1 : 1 type.

Potentiometric and Conductometric Titrations.—The potentiometric titration curves of H-bentonite show a monobasic acid character. The high base-exchange capacity (75-80 m. e. per 100 g.), calculated at the inflection point, and also the inflection between *p*H 7.0 and 8.5 suggest that the dominant clay mineral present in bentonite sample is montmorillonite (Mukherjee and Mitra, *J. Colloid Sci.*, 1946, **1,** 141). H-kaolin sample shows two inflection points in the *p*H curves—first one between *p*H 6.5 and 7.5 and the second one, between *p*H 7.5 and 10.0. The ratio of the total acids at the two inflection points is about 2.0. These features are known to be characteristic of kaolinites (Mukherjee and Mitra, *loc. cit.*). The potentiometric titration curves of the H-clay, isolated from illite sample, show three inflection points (Mitra and Rajagopalan, *Nature*, 1948, **162,** 104) at *p*H 7.3, 9.4, and 10.7 with KOH and at *p*H 6.8, 9.7, and 10.7 in case of $Ca(OH)_2$. The ratio of b. e. c.'s at the first and second inflexion points is between 1.5 and 1.9 and that of the second and third inflection is about 2.0. The conductometric titration curves of the H-clays with

bases show breaks at the corresponding concentrations of added bases where the potentiometric titration curves of the respective clays show inflection points.

Viscometric Titration.—The viscosity—base concentration curve of H-clay, prepared from bentonite, gradually increases to a maximum at about 70-80% neutralisation with KOH, and finally decreases with further addition of the base. In case of H-kaolin, viscosity gradually decreases tending to a more or less constant value, whereas viscosity of illite increases to a maximum at about 30-40% neutralisation and then falls to a constant value. The features of viscosity—base saturation curves of bentonite, kaolin, and illite samples used are the characteristics of montmorillonitie, kaolinite, and illite respectively.

Cationic Activity Measurements.—The variations in the K^+ ion activity and Ca^{2+} ion activity on the progressive addition of the corresponding bases to the H-clay show that kaolinite exhibits the highest dissociation, whereas ionisation from montmorillonite and illite is much less up to the neutralisation point. The divalent Ca^{2+} ion shows much less dissociation compared to K^+ ions in every case (Chatterjee, *loc. cit.*).

The results of X-ray, differential thermal and chemical analysis, potentiometric, conductometric, and viscometric titrations, and cationic activity measurements establish that the three clays, viz., bentonite, kaolin, and illite, may be regarded as pure montmorillonite, pure kaolinite, and pure illite respectively.

DISCUSSION

D. T. A. Curves of Binary Mixtures of Clay Minerals

Differential thermal analysis results of mixtures of kaolinite and montmorillonite, kaolinite and illite, and montmorillonite and illite have been presented in Figs. 1 to 3. For better comparison, curves of pure clay minerals have also been shown in the figures of the respective mixtures.

The D. T. A. data of mixtures of kaolinite and montmorillonite reveal that in the mixtures studied the individual constituents can easily be detected. The change in the height of the endothermic peak of kaolinite around 600°, the montmorillonite peak around 700° in kaolinite-montmorillonite mixture, and shifting of the peak temperature appear to depend on the percentage composition of the clay minerals present in the mixture, but a quantitative relation is not observed.

The results of differential thermal analysis of kaolinite-illite mixture show that the endothermic peak of kaolinite in the region of 600° and that of illite at 580° have merged to a single endothermic peak (cf. Grim *et al.*, *loc. cit.*) intermediate between 580° and 600°. As the percentage of kaolinite increases, the endothermic peak of illite around 890° becomes less pronounced. The common exothermic peak around 950-80° of kaolinite and illite mixture gradually shifts towards the illite peak temperature as the percentage of illite is gradually increased. Hence the presence of illite in kaolinitic clays could be detected from a consideration of the following factors: (*i*) the single and sharp endothermic peak near about the region of 600° should be far away from 600°, viz., towards 500°, (*ii*) the endothermic peak at 100-200° should be noticed, (*iii*) the single and sharp exothermic peak between 900 and 1000° should be much nearer to 900° than 1000°.

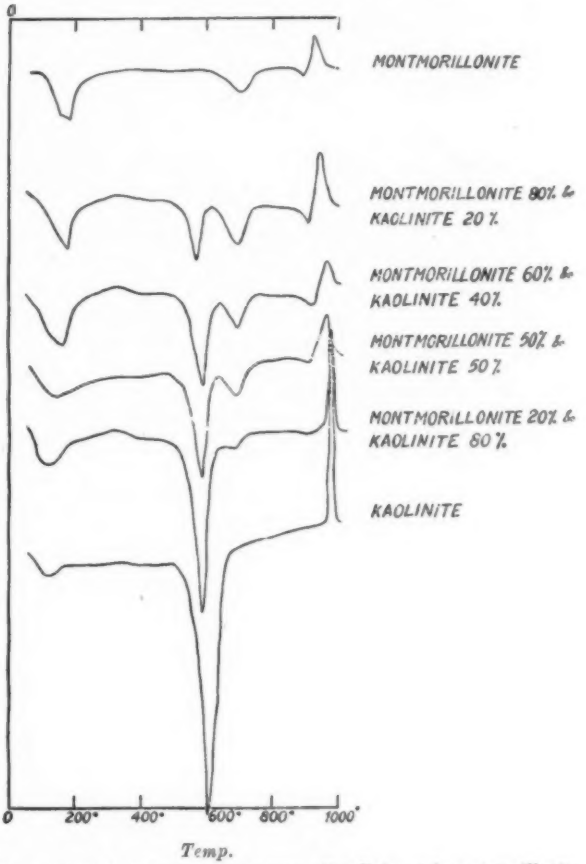

FIG. 1. D. T. A. diagrams of mixtures of kaolinite and montmorillonite.

The endothermic peak of illite at 580° and that of montmorillonite at 700-10° are separately and distinctly formed in the mixtures of montmorillonite and illite used. A marked shift in the peak temperatures has, however, been observed. The endothermic peak of illite at 580° has been seriously affected and maximum shifting of 40° has been noticed in the mixture containing 80% montmorillonite and 20% illite. The shifting of peak temperature has not been found to be proportional to the percentages of individual components in the mixture. Single exothermic peak for binary mixtures of illite and montmorillonite between 920° and 955° increases with gradual addition of illite to montmorillonite and decreases when montmorillonite is added to illite. An analysis of the D. T. A. data shows that the individual constituents can be detected within the range of components studied.

The potentiometric, conductometric, and viscometric titration curves and those of cationic activity measurements of the binary mixtures symbolised as pH, sp. cond., η, a_{K^+} or $a_{Ca^{2+}}$, have been presented in Figs. 4 to 7.

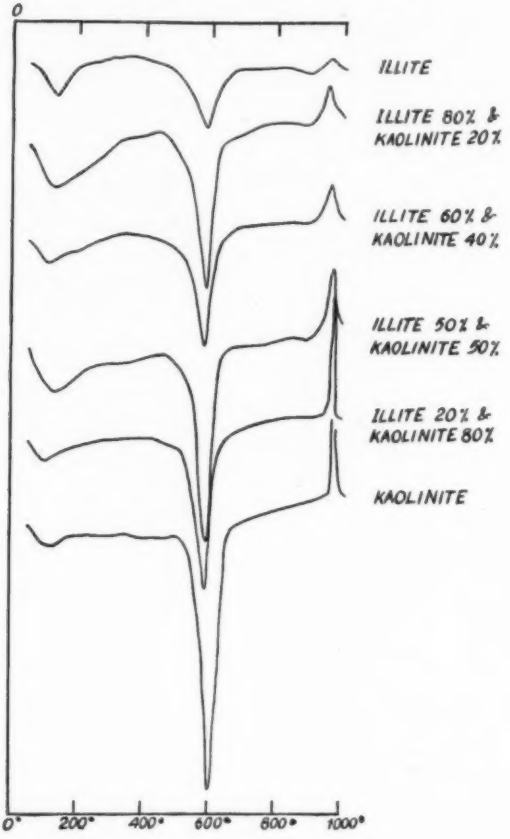

FIG. 2. D. T. A. diagrams of mixtures of kaolinite and illite.

Potentiometric Titration Curves of Binary Mixtures of Clay Minerals

The potentiometric titration curves of mixtures of H-kaolinite and H-montmorillonite show only one inflection point between *p*H 7.5 and 8.2. The three inflection points, namely, one for montmorillonite and two for kaolinite, seem to be merged into one. Taking the total acidity of H-kaolinite at the second inflection point and that at the first one of H-montmorillonite, the total acid, calculated on the basis of the weight percentages of the two ingredients, seems to approach the observed total acidity of the mixtures of H-kaolinite and H-montmorillonite (Table I). The potentiometric titration curves of mixtures of kaolinite and illite show two inflection points—the first one between *p*H 7.2 and 8.2 and the second one between *p*H 10.2 and 10.6. The ratio of b.e.c.'s at the two inflection points varies between 2.0 and 3.7. The two inflection points of H-kaolinite and the first two inflection points of H-illite seem to merge into one. The third inflection point of H-illite seems to be manifested just above *p*H 10.0 in the potentiometric titration curves of the mixtures.

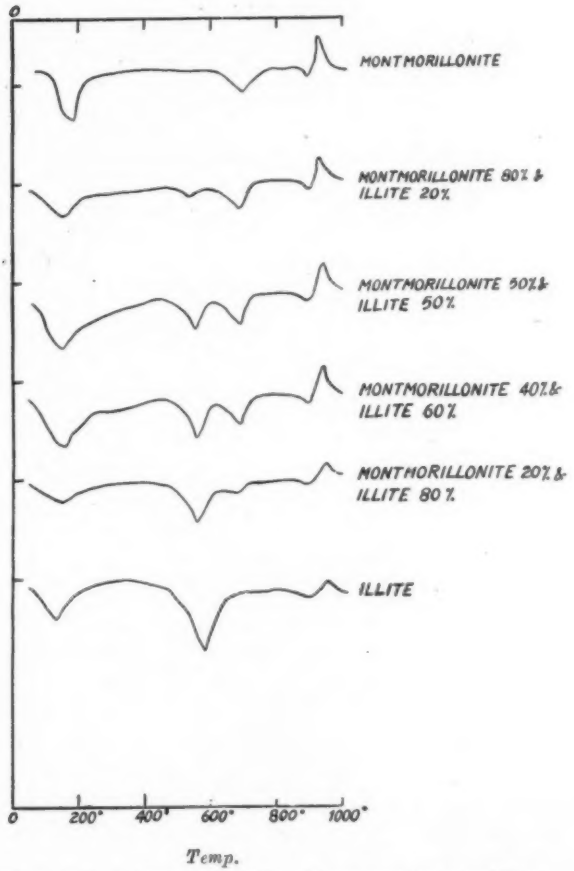

FIG. 3. D. T. A diagram of mixtures of montmorillonite and illite.

Calculated total acidity does not seem to show good correlation. Difficulty arises because in this case we have to take into account neutralisable acidities at five inflection points (two for kaolinites, three for illite) some of which seem to overlap one another in the mixture. The potentiometric titration curves of mixtures of H-montmorillonite and H-illite show two inflection points—the first one between *p*H 7.3 and 7.9 and the second one between *p*H 10.3 and 10.7. The ratio of b.e.c.'s at the inflection points is between 1.7 and 2.4. The first two inflection points of H-illite and that of H-montmorillonite appear to merge into one. The calculated total acidity and observed total acidity at the first inflection point seem to show a fair agreement. The presence of montmorillonite in montmorillonite-illite mixture brings about a considerable buffering around *p*H 10.0 and this seems to account for the very high total acidity as calculated from the second inflection point in the titration curves.

TABLE I

Total acidity of binary mixtures of clay minerals.

	Samples.	Base.	Total acid (m.e. per 100 g. of clay). Potentiometric curves. 1st inflection.	2nd inflection.	Conductometric curves. 1st break.	2nd break.
1.	Kaolinite & (80%)	KOH	21.0(8.1)*	..	29.5	..
	montmorillonite (20%)	$Ca(OH)_2$	24.0(7.5)	..	25.0	..
2.	Kaolinite & (50%)	KOH	47.0(8.1)	..	45.0	..
	montmorillonite (50%)	$Ca(OH)_2$	48.0(7.7)	..	47.0	..
3.	Kaolinite & (40%)	KOH	51.5(8.15)	..	54.0	..
	montmorillonite (60%)	$Ca(OH)_2$	57.0(7.6)	..	67.0	..
4.	Kaolinite & (20%)	KOH	74.0(8.2)	..	75.0	..
	montmorillonite (80%)	$Ca(OH)_2$	77.0(8.1)	..	81.0	..
5.	Kaolinite & (80%)	KOH	9.5(8.2)	25.0(10.3)	11.0	22.5
	illite (20%)	$Ca(OH)_2$	10.0(7.2)	37.0(10.25)	14.5	36.5
6.	Kaolinite & (50%)	KOH	16.5.(8.2)	46.0(10.25)	16.0	47.5
	illite (50%)	$Ca(OH)_2$	16.0(7.4)	55.0(10.4)	22.0	50.0
7.	Kaolinite & (40%)	KOH	19.0(8.1)	41.5(10.4)	19.0	37.5
	illite (60%)	$Ca(OH)_2$	20.0(7.5)	56.0(10.4)	28.0	42.5
8.	Kaolinite & (20%)	KOH	22.0(8.1)	53.0(10.6)	25.0	50.0
	illite (80%)	$Ca(OH)_2$	30.0(8.0)	63.0(10.4)	38.0	56.0
9.	Montomorillonite & (80%)	KOH	70.0(7.7)	135.0(10.55)	72.0	102.0
	illite (20%)	$Ca(OH)_2$	79.0(7.4)	136.0(10.7)	82.0	117.0
10.	Montmorillonite (50%)	KOH	51.0(7.5)	117.0(10.35)	61.0	90.0
	& illite (50%)	$Ca(OH)_2$	59.0(7.35)	116.0(10.4)	64.0	110.0
11.	Montmorillonite (40%)	KOH	47.0(7.9)	100.0(10.6)	52.0	72.0
	& illite (60%)	$Ca(OH)_2$	55.0(7.5)	107.0(10.6)	62.0	106.0
12.	Montmorillonite (20%)	KOH	35.0(7.7)	81.0(10.65)	40.0	76.5
	& illite (80%)	$Ca(OH)_2$	44.0(7.35)	105.0(10.35)	49.0	100.0

*Figures in parentheses denote *p*H at inflection.

Conductometric Titration Curves of Binary Mixtures of Clay Minerals

Specific conductance—base concentration curves of mixtures of kaolinite and montmorillonite show a single break at about the same m.e.'s of added base as in the inflection points of the corresponding *p*H curves of the mixtures. Specific conductance—base concentration curves of kaolinite and illite mixtures show two breaks. The total acids calculated at the breaks (Table I) in the conductometric curves, with the exception of a few instances, appear to show a fair agreement with those calculated at inflection points in the corresponding *p*H—base concentration curves. Mixtures of montmorillonite and illite show two

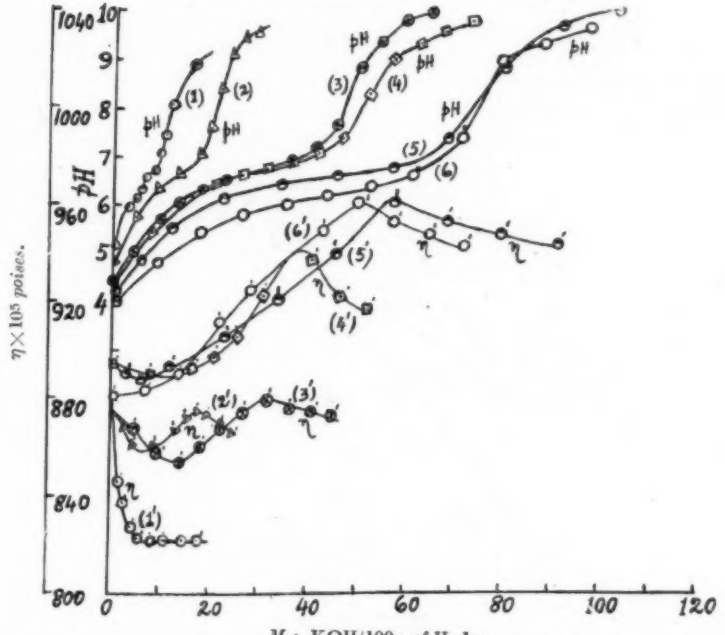

FIG. 4. Potentiometric and viscometric titration curves of mixtures of H-kaolinite and H-montmorillonite.

(1)&(1′): Kaolinite (K). (2)&(2′): 80%K+20%M. (3)&(3′): 50%K+50%M.
(4) & (4′): 40%K+60%M. (5)&(5′): 20%K+80%M. (6)&(6′): Montmorillonite (M).

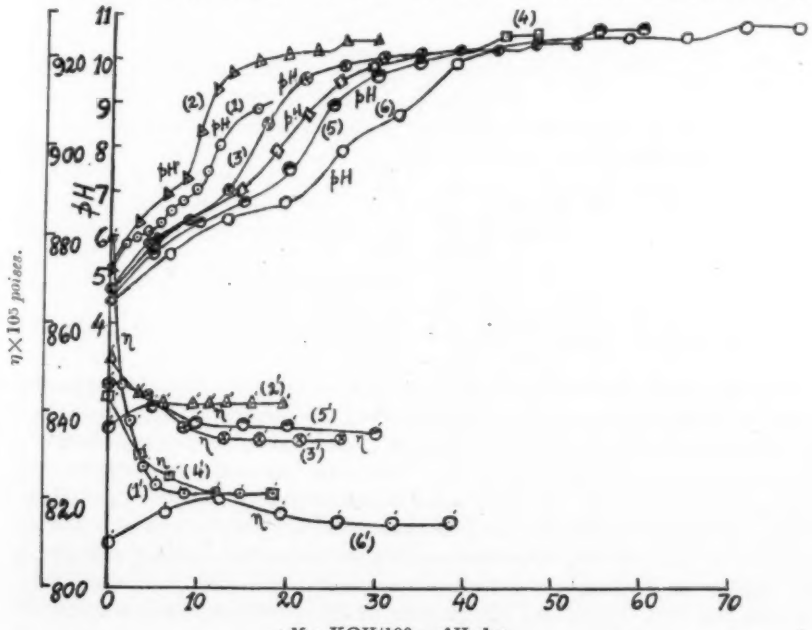

FIG. 5. Potentiometric and viscometric titration curves of mixtures of H-kaolinite and H-illite.

(1)&(1′): Kaolinite (K). (2)&(2′): 80%K+20%I. (3)&(3′): 50%K+50%I.
(4)&(4′): 40%K+60%I. (5)&(5′): 20%K+80%I. (6)&(6′): Illite (I).

breaks and total acids calculated from these breaks are shown in Table I. Summarising, calculated total acidity at the breaks and also number of breaks in the conductometric titration curves of the mixtures of clay minerals are in general agreement with the corresponding *p*H—base concentration curves.

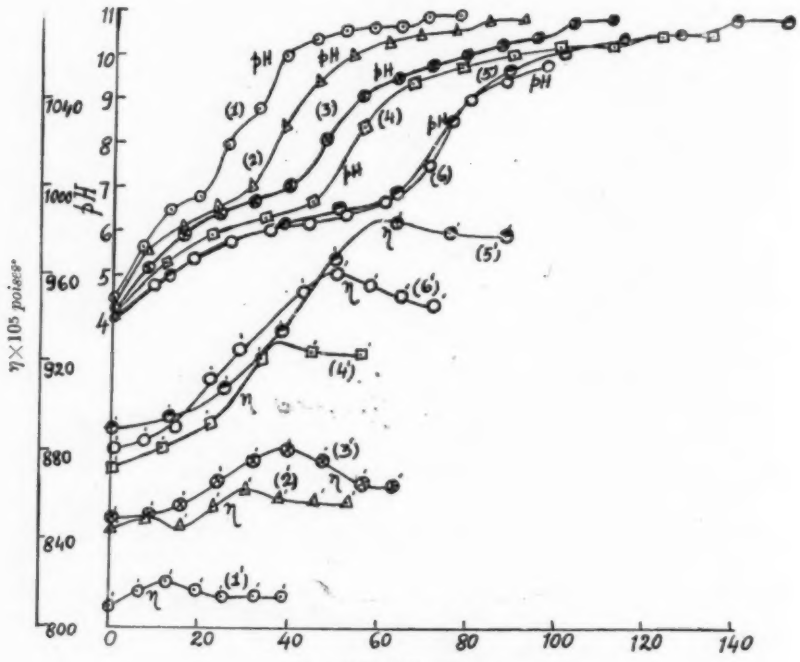

FIG. 6. Potentiometric and viscometric titration curves of mixtures of H-illite and H-montmorillonite.

(1) & (1′): Illite (I).
(2) & (2′): 80% I+20%M.
(3) & (3′): 60% I+40%M.
(4) & (4′): 50% I+50%M.
(5) & (5′): 20% I+80%M.
(6) & (6′): Montmorillonite (M).

Viscometric Titration Curves of Binary Mixtures of Clay Minerals

Viscosity—base saturation curves of mixtures of kaolinite and montmorillonite show the following features: (*i*) an initial fall in viscosity (characteristic of kaolinite), (*ii*) a rise to a maximum at about 70-80% neutralisation (characteristic of montmorillonite), (*iii*) a final fall in viscosity. An examination of the viscosity—base saturation curves shows that individual constituents can easily be detected in a mixture of montmorillonite and kaolinite. In case of kaolinite and illite mixtures, the maximum viscosity observed in the viscosity curve of H-illite around 30% neutralisation is absent when the mixture contains 40% or more of kaolinite. A binary mixture of montmorillonite and illite, containing 20% montmorillonite and 80% illite, shows two maxima in the viscosity—base saturation curve, the

first one at about 30% neutralisation due to illite and the second one at about 80% neutralisation due to montmorillonite. When the percentage of montmorillonite in the mixture is more than 20%, only one maximum in viscosity is observed at about 70-85% neutralisation. The position of maximum viscosity has been found to occur at different base saturations depending on the relative proportions of the two minerals.

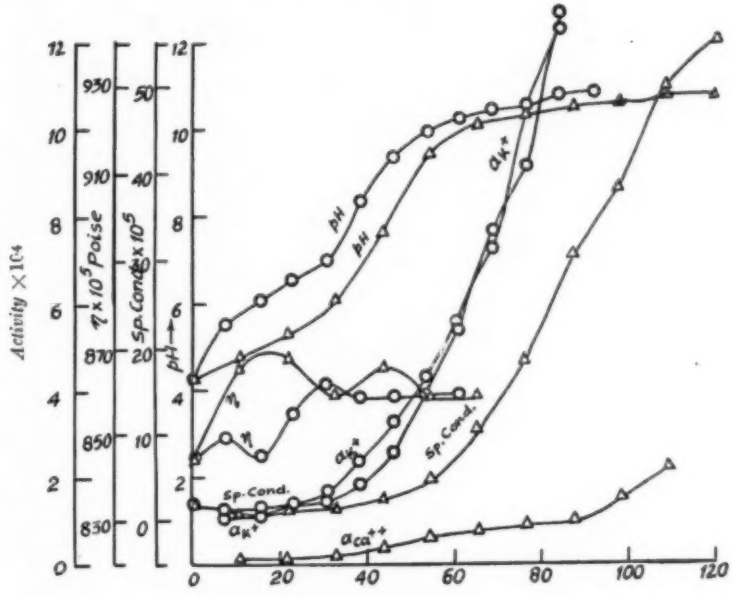

Fig. 7. *p*H, sp. cond., viscosity (η), and cationic activity curves.

(a_{K^+} and $a_{Ca_2^{++}}$) of a mixture of 80% H-illite and 20% H-montmorillonite.

O—H-clay+KOH.

Δ —H-clay+$Ca(OH)_2$.

K^+ *and* Ca^{2+} *Activity of Binary Mixtures of Clay Minerals*

Fractions active of K^+ and Ca^{2+} in relation to degree of cation saturation of binary mixtures of clay minerals have been calculated from activity—base saturation curves and presented in Table II. It appears that the dissociation of cations (K^+, Ca^{2+}) from the mixtures of clay minerals depends on the nature and relative proportions of the clay minerals present in them. Mixtures containing higher percentages of kaolinite show higher dissociation of K^+ ions. Any other conclusion based on the cation activity measurements will be too premature at this stage.

TABLE II

Fractions active of K^+ *and* Ca^{2+} *of clay minerals in mixtures in relation to cation saturation.*

	Samples.	Assumed. (m.e.100g.)	Cation.	Fraction active of cations saturated at 25%.	50%.	75%.	100%.	125%.
1.	Kaolinite & (80%)	21	K^+	0.230	0.120	0.100	0.110	0.120
	montmorillonite(20%)	24	Ca^+	0.033	0.016	0.022	0.026	0.026
2..	Kaolinite & (50%)	47	K^+	0.110	0.060	0.050	0.060	0.080
	montmorillonite(50%)	48	Ca^{2+}	0.025	0.008	0.005	0.009	0.018
3.	Kaolinite & (40%)	51.5	K^+	0.15	0.08	0.060	0.060	0.09
	montmorillonite(60%)	57	Ca^{2+}	0.03	0.01	0.005	0.007	0.01
4.	Kaolinite & (20%)	74	K^+	0.108	0.060	0.050	0.060	0.080
	montmorillonite(80%)	77	Ca^{2+}	0.031	0.007	0.003	0.005	0.014
5.	Kaolinite & (80%)	9.5	K^+	0.50	0.290	0.25	0.290	0.290
	illite (20%)	10	Ca^{2+}	0.16	0.068	0.05	0.046	0.048
6.	Kaolinite & (50%)	16.5	K^+	0.34	0.200	0.190	0.230	0.230
	illite (50%)	16	Ca^{2+}	0.10	0.045	0.033	0.035	0.335
7.	Kaolinite & (40%)	19	K^+	0.33	0.22	0.18	0.20	0.23
	illite (60%)	20	Ca^{2+}	0.08	0.02	0.02	0.03	0.04
8.	Kaolinite & (20%)	22	K^+	0.22	0.130	0.120	0.120	0.14
	illite (80%)	30	Ca^{2+}	0.10	0.026	0.026	0.033	0.04
9.	Montmorillonite (80%)	70	K^+	0.150	0.100	0.070	0.060	0.100
	& illite (20%)	79	Ca^{2+}	0.005	0.002	0.005	0.007	0.012
10.	Montmorillonite (50%)	51	K^+	0.12	0.070	0.060	0.078	0.100
	& illite (50%)	59	Ca^{2+}	0.04	0.004	0.004	0.003	0.005
11.	Montmorillonite (40%)	47	K^+	0.16	0.110	0.09	0.100	0.12
	& illite (60%)	55	Ca^{2+}	0.09	0.014	0.01	0.014	0.02
12.	Montmorillonite (20%)	35	K^+	0.240	0.120	0.110	0.114	0.130
	& illite (80%)	44	Ca^{2+}	0.018	0.009	0.009	0.017	0.021

CONCLUSION

Identification of the clay mineral components present in mixtures requires careful consideration of (*i*) the features of the potentiometric and conductometric titration curves, (*ii*) the variations in viscosity with increasing addition of bases, (*iii*) the number of inflection points in the potentiometric titration curves and/or breaks in the conductometric titration curves, (*iv*) the *p*H at inflection, (*v*) the ratio of total acids at inflection, (*vi*) the number of maxima in the viscosity—base concentration curves as also the percentage neutralisation at which viscosity—base concentration curves show maximum or maxima, (*vii*) the peak temperatures in the D. T. A. curves, (*viii*) the peak heights, and (*ix*) the shifting of the peak temperatures. Conclusions drawn on the basis of measurement of any single property may often lead to erroneous results as one clay mineral component may exert a marked influence on that property of the other in the mixture and mask the presence of the latter.

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Studies on the Bacterial Decomposition of Humic Acid in the Clay-humus Mixtures

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Stabilisation of humus by its possible interaction with the clay minerals has been sought from a study of the bacterial decomposition of humus alone and in combination with clays. The rate of bacterial decomposition of humic acid has been found to be decreased when it is mixed with clay minerals with or without the presence of the metal ions. The humic acid has thus been stabilised by combining with the negative clay micelles through H^+ or metal ion bonding, the latter being stronger than the former.

Due to the complex nature of humus, its interaction with clays cannot be conveniently studied by means of ordinary chemical methods. Some physico-chemical methods, viz., studies on base-exchange capacity, adsorption, and viscosity, were used for this purpose, the detailed results of which have been given in the previous communications (*Indian J. Appl. Chem.*, 1960, **23**, 145, this *Journal*, 1960, **37**, 793). Since humic acid is also amenable to biological methods for its estimation, this line of investigation is likely to hold promise. From the investigation of Ensminger and Gieseking (*Soil Sci.*, 1942, **53**, 205) and Erickson (Ph.D. thesis, University of Illinois, 1948), it has been found that the decay characteristics of some organic materials are often quite different in free as compared to that adsorbed by clay minerals. The increased resistivity of humus, when adsorbed by the clay minerals, to biological decomposition was first observed by Waksman ("Humus: Origin, Chemical Composition, and Importance in Nature") because of the fact that the humus content in a clay-rich soil can be more easily built than in a clay-poor soil. An answer as to whether this is so because of the stabilisation of humus by its possible interaction with the clay, has been sought from a study of the bacterial decomposition of humus alone and in combination with clays. Conversely, the resistance to bacterial decomposition has been used to furnish a measure of the extent of clay-humus interaction. In the present work the rate of bacterial decomposition of crude humic acid fraction has been compared with that adsorbed by montmorillonite and illite as clay-humic acid complexes in presence of H^+ and Al^{3+} ions.

EXPERIMENTAL

The bacterial decomposition has been followed according to the following scheme. In a large pyrex conical flask a thorough mixture of about 200g. of washed white sand, humic acid sol to supply about 150 mg. of carbon, a few c. c. of a solution containing K_2HPO_4, $MgSO_4$, a trace of $FeCl_3$, and a few drops of garden soil suspension, which supplied the necessary bacteria for decomposition, was taken. The mixture was kept just moist, care being taken to prevent any water-logging at the surface of the sand. In the case of clay-humus-Al^{3+} mixture, the medium was, however, made free of free acid (and hence possibly of Al^{3+}) before mixing with the sand and the suitable nutrients to maintain the bacterial

activity. Gradually with time humic acid decomposed; the evolved CO_2 gas was drawn out of the conical flask by a current of dry and CO_2-free air and was absorbed in a known volume of $N/10$-$Ba(OH)_2$ solution. The excess of baryta was then titrated with standard oxalic acid. The process was followed at an interval of 24 hours and the amount of CO_2 evolved was expressed in terms of volume difference of $N/10$ oxalic acid between the initial reading and the reading obtained after CO_2 absorption. The same experiment under identical conditions was then performed with the clay-humic acid mixtures. In all cases the experiments were checked with a control where all but humic acid were taken. The results are recorded in Tables I to III and shown graphically in Figures 1 and 2.

TABLE I

*Bacterial decomposition of SHm.**

Amount of humic acid in 40c.c. = 0.24g.

	Humic acid.		Blank control.	
Time (days).	Vol. of $N/10$ oxalic acid to neutralise 30 c. c. of 1.17$N/10$-$Ba(OH)_2$ soln.	Diff. between successive days.	Vol. of $N/10$ oxalic acid to neutralise 30 c. c. of 1.17 $N/10$-$Ba(OH)_2$ soln.	Diff. between successive days.
0	35.1 c.c.	..	35.1 c.c.	..
1	32.6	2.5 c.c.	34.2	0.90c.c.
2	33.3	1.8	34.8	0.30
3	33.6	1.5	34.8	0.30
4	34.0	1.1	34.9	0.20
6	34.1	1.0	34.95	0.15
8	34.2	0.9	35.0	0.10
10	34.5	0.6	35.1	Nil
Total		9.4±0.2		1.95±0.2

*SHm = Humic acid extracted from Siliguri soil.

TABLE II

*Bacterial decomposition of CI clay — SHm mixture.**

Humic acid in the mixture : clay = 1:20.

Amount of humic acid in soln. = 0.24 g.

	Contai clay/humic acid mixture.		Contai clay/humic acid mixture in presence of Al^{3+} ion.	
Time (days).	Vol of $N/10$ oxalic acid to neutralise 30 c.c. of 1.16$N/10$-$Ba(OH)_2$ soln.	Diff. between successive days.	Vol of $N/10$ oxalic acid to neutralise 30 c.c. 1.16$N/10$-$Ba(OH)_2$ soln.	Diff. between successive days.
0	34.8 c.c.	..	34.8 c.c.	..
1	32.4	2.4 c.c.	33.0	1.8 c.c.
2	33.2	1.6	33.7	1.1
3	33.6	1.2	33.9	0.9
5	33.6	1.2	34.2	0.6
7	33.9	0.9	34.2	0.6
10	34.1	0.7	34.5	0.3
Total		8.0±0.2		5.3±0.2

*CI clay = Illitic clay from Contai soil.
SHm = Humic acid from Siliguri soil.

TABLE III

*Bacterial decomposition of AGM clay—SHm mixture.**

In the mixture humic acid : clay = 1 : 20.
Amount of humic acid = 0.24g.

Time (days).	Montmorillonite clay—humic acid mixture. Vol. of $N/10$ oxalic acid to neutralise 30 c.c. of $1.19N/10$-$Ba(OH)_2$ soln.	Difference between successive days.	Montmorillonite clay—humic acid mixture in peresence of Al^{3+} ion. Vol of $N/10$ oxalic acid to neutralise 30 c.c. $1.19N/10$-$Ba(OH)_2$ soln.	Difference between successive days.
0	35.6 c.c.	..	35.6 c.c.	..
1	33.4	2.2. c.c.	34.0	1.6 c.c.
2	34.4	1.3	34.5	1.1
3	34.6	1.0	34.8	0.8
5	34.8	0.9	35.0	0.6
7	35.0	0.6	35.2	0.4
10	35.1	0.5	35.4	0.2
Total		6.5 ± 0.2		4.7 ± 0.2

*AGM = Montmorillonite clay from aquagel.
SHm = Humic acid from Siliguri soil.

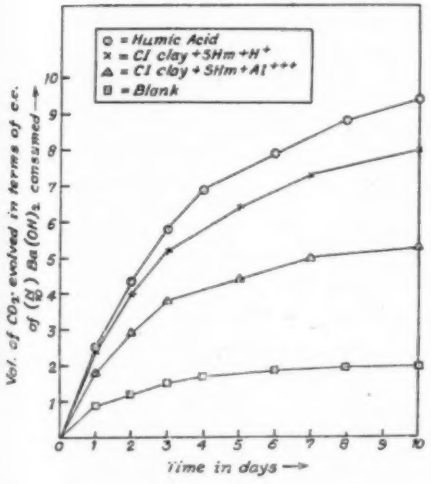

FIG. 1. Bacterial decomposition of Cl clay—SHm mixtures.

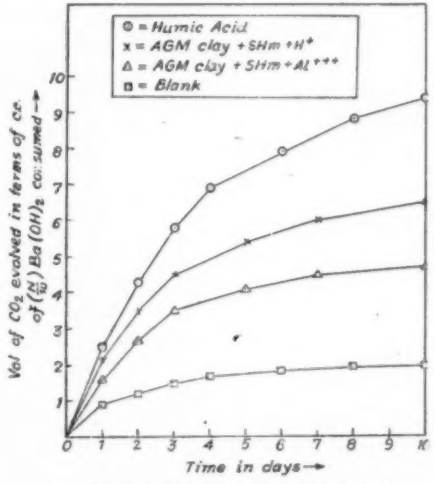

FIG. 2. Bacterial decomposition of AGMclay—SHm mixtures.

DISCUSSION

Humic acid can be decomposed quantitatively by strong oxidising agents like $KMnO_4$, $K_2Cr_2O_7$, or H_2O_2 in acid medium. This effect permits us to estimate the organic matter even when it remains combined with clay materials, because humic acid adsorbed on clay cannot resist oxidation by these strong oxidising agents. The bacterial oxidation, on the other hand, is a very slow process and is not so drastic. Hence in Figs. 1 and 2 the study of

the bacterial oxidation has particularly shown that the rate of decomposition of humic acid is decreased when it is mixed with clay minerals. This resistance towards oxidation is greater in case of montmorillonite-humic acid complex than illite-humic acid complex. In presence of metal ion like Al^{3+}, the decomposition of humic acid is further checked. This may be attributed to an adverse effect of Al^{3+} ions on bacterial activity. No bacterial counting was, however, done in the present experiments. It must be pointed out that the Al^{3+} content will indeed be very small under the conditions of the experiments. So it can be anticipated that clay and humic acid have been united in such a way that the easily oxidisable groups of humic acid are not available for bacterial decomposition. In other words, the humic acid has been stabilised by combining with the negative clay micelles through H^+ or metal ion bonding, the latter being stronger than the former.

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Acid Dissociation Constants of the N^1-substituted Biguanides and Dibiguanides

R. L. Dutta and Nihar Ranjan Sengupta

Acid dissociation constants of some of the N^1-substituted biguanides and dibiguanides have been determined by Bjerrum's method and the influence of the substitutions in the biguanide molecule on its basic character has been discussed.

Das Sarma (this *Journal*, 1952, **29**, 217) and also Sengupta and Rây (*ibid.*, 1960, **37**, 303) have determined the acid dissociation constants (basic strength) of biguanide and several N^1-substituted biguanides and N^1N-dibiguanides. The determination of the acid dissociation constant of some N^1-substituted biguanides, not previously examined, have been described here. This affords a wider range of a comparative study of the influence of substituted groups in N^1-position of the biguanide on their basic properties.

Being diacidic bases, N^1-substituted biguanides can combine with one or two H^+ to form conjugated acids, R-BigH$_2^+$ and R-BigH$_3^{2+}$ corresponding to the salts R-BigH.HX and R-BigH.2HX(where R-BigH=one molecule of N^1-substituted biguanide and HX= a monobasic acid).

Therefore,

$$\text{R-BigH}_2^+ \rightleftharpoons \text{R-BigH} + \text{H}^+$$

and

$$\text{R-BigH}_3^{2+} \rightleftharpoons \text{R-BigH}_2^+ + \text{H}^+.$$

Hence k_{a_1} and k_{a_2} may be represented (Das Sarma, *loc. cit.*) as

$$k_{a_1} = \frac{[\text{R-BigH}]\ [\text{H}^+]}{[\text{R-BigH}_2^+]}$$

and

$$k_{a_2} = \frac{[\text{R-BigH}_2^+]\ [\text{H}^+]}{[\text{R-BigH}_3^{2+}]}.$$

The values of k_{a_1} and k_{a_2} are obtained from the formation curves (Fig. 1)* obtained by plotting $\bar{\eta}$ against the *p*H values when $\bar{\eta}$ =0.5 and 1.5 respectively (cf. Bjerrum, "Metal Ammine Formation in Aqueous Solutions", P. Haase and Sons, Copenhagen, 1941; Das Sarma, *loc. cit.*).

*Only a few representative curves have been presented.

Hexamethylenedibiguanide, on the other hand, forms salts of the type, $[Hex(BigH)_2].4HX$, showing a maximum acidity of four. Hence the reaction between the base and the proton may be represented as:

$$AH^+ \rightleftharpoons A + H^+ \qquad \therefore \quad k_{a_1} = \frac{[A]\,[H^+]}{[AH^+]}$$

$$AH_2^{2+} \rightleftharpoons AH^+ + H^+ \qquad \therefore \quad k_{a_2} = \frac{[AH^+]\,[H^+]}{[AH_2^{2+}]}$$

$$AH_3^{3+} \rightleftharpoons AH_2^{2+} + H^+ \qquad \therefore \quad k_{a_3} = \frac{[AH_2^{2+}]\,[H^+]}{[AH_3^{3+}]}$$

$$AH_4^{4+} \rightleftharpoons AH_3^{3+} + H^+ \qquad \therefore \quad k_{a_4} = \frac{[AH_3^{3+}]\,[H^+]}{[AH_4^{4+}]}$$

where $A = C_6H_{12}(C_2N_5H_6)_2$ and AH^+, AH_2^{2+}, AH_3^{3+}, and AH_4^{4+} are the ions of the mono-, di-, tri- and tetra-acid salts respectively. The values of k_{a_1}, k_{a_2}, k_{a_3}, and k_{a_4} are obtained from the formation curve (Fig. 2) where $\bar{\eta}$ =0.5, 1.5, 2.5, and 3.5 respectively (cf. Das Sarma, *loc. cit.*).

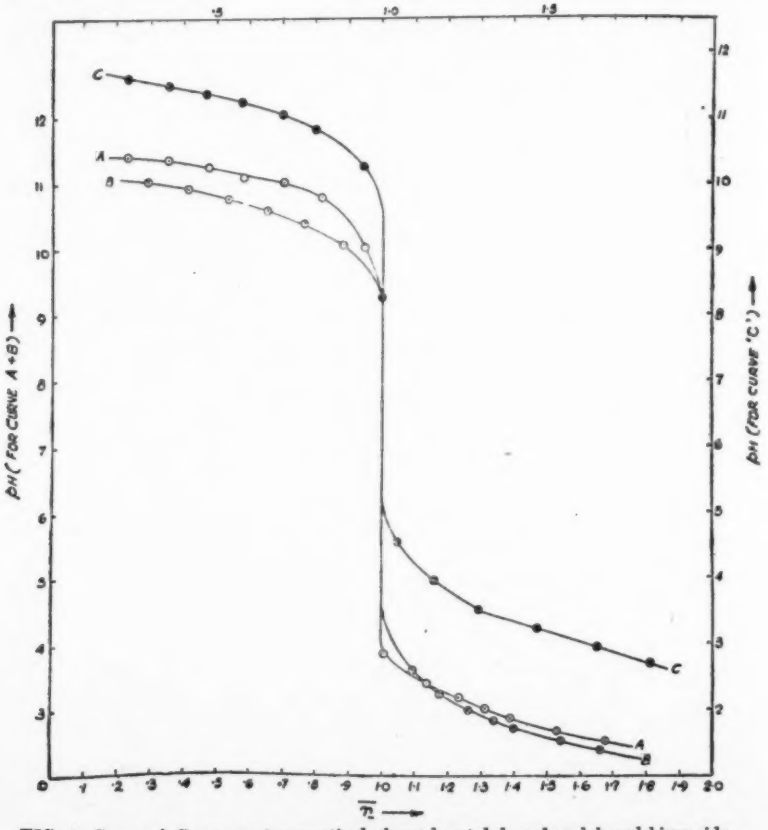

FIG. 1. Curves A-C represent respectively benzyl, *p*-tolyl, and cyclohexyl-biguanide.

These values can also be obtained from the following relations (cf. Das Sarma, *loc. cit.*):

1. When $(C_H - C'_H) < C_A$ and the formation of cationic acid higher than AH^+ being negligible, we have $k_{a_1} = \frac{[C_A - C_H + C'_H]}{[C_H - C'_H]} \cdot [H^+]$

2. When $(C_H - C'_H) > C_A < 2\,C_A$, we have $k_{a_2} = \frac{[2C_A - C_H + C'_H]}{[C_H - C'_H - C_A]} \cdot [H^+]$

([A] and acids higher than AH_2^{2+} may be neglected).

3. Similarly, when $(C_H - C'_H) > 2\,C_A < 3\,C_A$, we have $k_{a_3} = \frac{[3C_A - C_H + C'_H]}{[C_H - C'_H - 2C_A]} \cdot [H^+]$

4. When $(C_H - C'_H) > 3C_A < 4C_A$, we have $k_{a_4} = \frac{[4C_A - C_H + C'_H]}{[C_H - C'_H - 3C_A]} \cdot [H^+]$

where C_H=concentration of the total acid added, C'_H=concentration of the total acid present in the mixture at equilibrium (obtained from pH values), and C_A=total ligand taken.

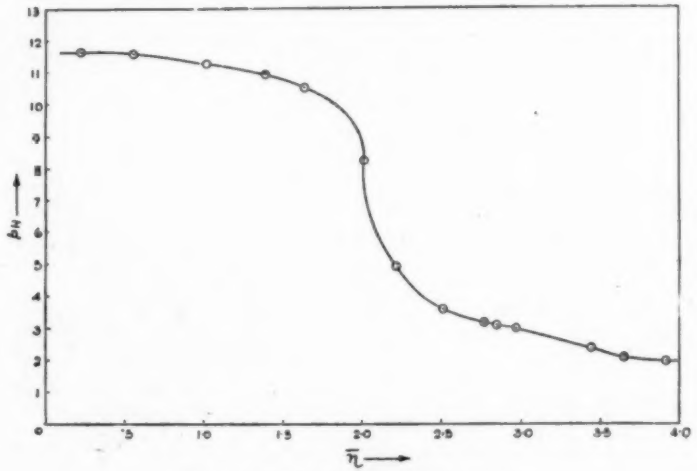

FIG. 2. Hexamethylenedibiguanide.

The acid dissociation constant values of these biguanides are recorded in Tables II and III for comparison. On comparing the value of the first acid dissociation, k_{a_1} (basic strength), of the biguanide and substituted biguanides, it may be concluded that biguanide and its N^1-mono- or dialkylbiguanides are stronger bases than the aryl-substituted ones. Benzylbiguanide behaves like alkylbiguanides in this respect. This also holds good of the cyclohexylbiguanide. On the contrary, *p*-tolyl- and phenetylbiguanides have values similar to phenylbiguanides. In the case of the dibiguanides, the ethylene- and hexamethylene-dibiguanides are stronger bases than the *m*-phenylenedibiguanide.

The alkylbiguanides may be arranged in the ascending order of their basic character as: butyl^n<propyl^n=propyl^i<ethylhexyl<hexyl^n=methyl<ethyl<dimethyl<diethyl.

The hydroxyl group, when present in the alkyl radical, increases the basicity of the ligand, whereas the methoxyl group present in the same position as that of the hydroxyl group decreases the basicity and shows almost the same value of k_{a_1} as that of the corresponding alkylbiguanide (Sengupta and Rây *loc. cit.*).

EXPERIMENTAL

Propyl^n -, propyl^i -and butyl^n -biguanide acid sulphates were obtained by heating the requisite amine, dicyandiamide, and copper sulphate on a water bath, treating with H_2SO_4 (dil.), then with H_2S, and finally by concentration and cooling.

TABLE I

Materials	Found. N.	Found. Anion.	Found. H_2O.	Calculated. N.	Calculated. Anion.	Calculated. H_2O.
1. Propyl^n biguanide acid sulphate, $C_3H_7.C_2N_5H_6.H_2SO_4$	28.96%	39.62%	..	29.05%	39.83	..
2. Propyl^i biguanide acid sulphate, $C_3H_7.C_2N_5H_6.H_2SO_4.H_2O$	27.45	37.40	..	27.13	37.20	..
3. Butyl^n biguanide acid sulphate, $C_4H_9.C_2N_5H_6.H_2SO_4$	27.20	37.44	..	27.45	37.65	..
4. Hexyl^n biguanide sulphate, $(C_6H_{13}.C_2N_5H_6)_2.H_2SO_4.2H_2O$ (Dutta, *Z. anorg. Chem.*, 1959, **302**, 237)	27.45	19.06	7.12	27.78	19.01	7.14%
5. 2-Ethylhexylbiguanide acid sulphate, $(C_8H_{18}.C_2N_5H_6).H_2SO_4.1.5H_2O$ (Dutta and Lahiry, Z. *anorg. Chem.*, in press).	20.95	28.13	8.48	20.71	28.40	8.00
6. Cyclohexylbiguanide acid sulphate, $(C_6H_{11}.C_2N_5H_6).H_2SO_4$ (Dutta and Lahiry, *loc.cit.*)	25.17	34.58	..	24.91	34.16	..
7. *p*-Tolylbiguanide hydrochloride, $C_7H_7.C_2N_5H_6.HCl$ (Ghosh and Chatterjee, this *Journal*, 1955, **32**, 222)	..	15.75	..	15.60	—	..
8. Benzylbiguanide acid sulphate, $C_7H_7.C_2N_5H_6.H_2SO_4$ (Rây, *Z. anorg. Chem.*, in press)	..	33.01	..	..	33.33	..
9. *p*-Pheatylbiguanide hydrochloride $C_8H_9O.C_2N_5H_6.HCl$ (Ghosh and Banerjee, this *Journal*, 1955, **32**, 32)	..	13.82	..	..	13.78	..
10. Hexamethylenedibiguanide acid sulphate, $(C_6H_{12}.C_4N_{10}H_{12}).2H_2SO_4$ (Dutta, this *Journal*, 1960, **37**, 32)	27.89	38.29	3.15	28.11	38.55	3.61

The biguanide hydrochloride solutions were prepared from their corresponding sulphate and $BaCl_2$ solution in calculated quantities. All of these were of 0.05*M* strength with respect to the ligand concerned.

Alkali solutions used were prepared from caustic soda of Merck's analytical variety with a little $BaCl_2$ solution to remove any carbonate present. The alkali solutions were standardised against dried hydrazine sulphate. Hydrochloric acid solution was standardised against standard alkali and also by determination of chlorine as AgCl. All the vessels employed were of Jena glass and all solutions were made with conductivity water.

Procedure.—0.05*M* Biguanide hydrochloride solution (10 c.c.) was taken in each of a number of 50 c.c. volumetric flasks and varying amounts of standard HCl or alkali solutions were added to the flasks; the volume was made to 50 c.c. The flasks containing the solutions were kept for 24 hours at 30°±2°. The values of the solutions were measured by using universal glass electrode (Cambridge) against a saturated calomel reference electrode. The values of k_{a_1} and k_{a_2} were obtained from the $\bar{\eta}$ values plotted against *p*H. The results are recorded in Table II, which also includes the corresponding values of other ligands previously studied.

TABLE II

Acid dissociation constants of hexamethylenedibiguanide.

C_A=.005*M* Temp.=32°±2°

C_H.	*p*H.	C'_H.	$C_H-C'_H$.	$\bar{\eta}$.	Acid dis. const.
I. $(C_H-C'_H) < (C_A)$.					
0.00112*M*	11.71	..	0.00112*M*	0.22	7.80×10^{-12}*
0.00171	11.61	..	0.00171	0.34	4.61×10^{-12}
0.00230	11.55	..	.. 0.00230	0.46	k_{a_1} 3.36×10^{-12}
0.00289	11.50	..	0.00289	0.58	2.39×10^{-12}
0.00348	11.41	..	0.00348	0.70	1.71×10^{-12}
II. $(C_H-C'_H) > C_A < 2C_A$.					
0.00584	11.15	..	0.00584	1.17	3.48×10^{-11}*
0.00643	11.06	..	0.00643	1.28	2.17×10^{-11}
0.00702	10.92	..	0.00702	1.40	k_{a_2} 1.80×10^{-11}
0.00761	10.75	..	0.00761	1.52	1.62×10^{-11}
0.00820	10.65	..	.. 0.00820	1.64	1.30×10^{-11}
III. $(C_H-C'_H) > 2C_A < 3C_A$.					
0.01065	8.24	..	.. 0.010560	2.11	..*
0.01174	6.75	..	0.011740	2.35	..*
0.01233	3.60	0.000251	0.012079	2.42	12.5×10^{-4}
0.01292	3.52	0.000302	0.012620	2.52	k_{a_3} 12.7×10^{-4}
0.01351	3.38	0.000417	0.013093	2.62	12.6×10^{-4}
0.01646	2.66	0.002188	0.014272	2.85	13.7×10^{-4}
0.01764	2.53	0.002951	0.014689	2.94	..*
IV. $(C_H-C'_H) > 3C_A < 4C_A$.					
0.02000	2.46	0.003467	0.016533	3.30	7.91×10^{-3}
0.02100	2.40	0.003981	0.017021	3.41	5.88×10^{-3}
0.02401	2.26	0.005495	0.018513	3.70	k_{a_4} 2.37×10^{-3}
0.02637	2.14	0.007079	0.019293	3.86	1.14×10^{-3}
0.02856	2.06	0.008710	0.019785	3.95	..*

	k_{a_1}.	k_{a_2}.	k_{a_3}.	k_{a_4}.
Graphical ..	2.88×10^{-12}	1.78×10^{-11}	3.2×10^{-4}	5.25×10^{-3}
Calculated ..	3.00×10^{-12}	1.72×10^{-11}	3.1×10^{-4}	4.32×10^{-3}

N.B. In taking the mean of the calculated k_a values we have omitted the border line values (marked*).

TABLE III

Biguanides.	$k_{a1}\times10^{12}$.	$k_{a2}\times10^{3}$.	Reference.
1. Unsubstituted	3.02	1.167	Das Sarma
2. Methyl	3.63	1.000	,,
3. Ethyl	3.39	0.832	,,
4. Dimethyl	3.02	1.69	,,
5. Diethyl	2.09	2.93	,,
6. Propyl^{n}	4.47	0.79	Present authors
7. Propyl^{i}	4.47	0.79	,,
8. Butyl^{n}	5.25	1.20	,,
9. Hexyl^{n}	3.63	0.55	,,
10. Ethylhexyl	3.98	0.79	,,
11. Cyclohexyl	4.07	0.63	,,
12. Ethanol	2.98	1.58	Sengupta and Rây
13. Propanol	3.16	1.00	,,
14. Methoxyethyl	3.38	1.00	,,
15. Methoxypropyl	3.98	0.83	,,
16. Phenyl	19.05	6.92	Das Sarma
17. Benzyl	5.62	1.99	Present authors
18. *p*-Tolyl	14.40	2.51	,,
19. *p*-Phenetyl	15.10	1.99	,,
20. α-Naphthyl	5.75	8.85	Das Sarma

Dibiguanides.	k_{a1}.	k_{a2}.	k_{a3}.	k_{a4}.	
1. Ethylene	1.74×10^{-12}	4.57×10^{-12}	1.32×10^{-3}	1.82×18^{-2}	Das Sarma
2. Hexamethylene	2.88×10^{-12}	1.78×10^{-11}	0.32×10^{-3}	5.25×10^{-3}	Present authors
3. *m*-Phenylene	4.07×10^{-12}	1.35×10^{-10}	7.03×10^{-3}	3.92×10^{-2}	Das Sarma

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Complex Compounds of Substituted Thioureas. Part I. Copper Derivatives of *N*-Acetylthiourea, *S*-Acetylthiourea and *N*-Phenylthiourea

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Several complex compounds of *N*-acetyl. *S*-acetyl-, and N-phenyl-thioureas with copper salts have been prepared and their properties studied.

Addition compounds of thiourea with metallic salts have been studied from very early times, notably by Maly, Claus, Rathke, Rosenheim, Kohlschutter and others (Beilstein, "Handbuch der organischen Chemie", 1921, Band III, syst. No. 216, p. 185). Little work has, however, been done till now on the compounds of substituted thioureas with metallic salts and only studies in this direction appear to be the following.

(1) CuCl, 3PhTh, $3H_2O$ (Rathke, *Ber.*, 1884, **17**, 297).

(2) $CuSO_4$, 2AcTh (Seidler, *J. prakt. Chem.*, 1880, *ii*, **21**, 140).

(3) Several compounds of ethylenethiourea with metallic ions, viz., Cu^+, Ag^+, Au^+, Pd^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+}, (Morgan and Burstall, *J. Chem. Soc.*, 1928, 143).

(4) Several copper compounds with thiourea and substituted thiourea in which copper has been represented as bivalent (Dehn, *J. Amer. Chem. Soc.*, 1940, **62**, 3189).

(5) Cu_2SO_4, 6PhTh; Cu_2SO_4, 3PhTh; Cu_2Cl_2, 2PhTh; Cu_2Cl_2, 3PhTh (Sahasrabudhey and Krall, this *Journal*, 1942, **19**, 25).

(N. B. PnTh and AcTh stands for $C_6H_5NHCSNH_2$ and $CH_3CONHCSNH_2$ respectively).

It will be seen that in the metal-thiourea complexes, any particular metal ion shows a great diversity in the co-ordination number and in many cases fractional molecules of thioureas per metal ion are present. For example, in the case of copper, nine classes of thiourea complexes have been reported (including the present work), viz., (1) M:RTh=1:4 (Morgan and Burstall, *loc. cit.*); (2) M:RTh=1:3 (Rathke, *loc. cit.*); (3) M:RTh=1:2.5 (Kohlschutter and Brinttlebank, *loc. cit.*); (4) M:RTh=1:2.33 (Kohlschutter, *loc. cit*).; (5) (M:RTh=1:2.2 (Kohlschutter *et al.*, *loc. cit.*); (6) M:RTh=1:2 (Kohlschutter *et.al.*, *loc. cit.*); (7) M:RTh=1:1.75 (present work); (8) M:RTh=1:1.5 (present work); (9) M:RTh=1:1 (Rathke, *loc. cit.*).

Of these nine types, a few compounds of the types (1), (2), (3), (6), (7), (8), and (9) have been obtained in the present work. Types (2), (6), and (9) can be taken as definite compounds and not mixtures, as a large number of compounds of each of the types (2) and (6) can be obtained in various ways, and as type (9) has the lowest thiourea content. The only compound of the type (1) $CuNO_3$, 4 ethylenethiourea (Morgan and Burstall, *loc. cit.*)

seems to be a definite compound since it has been prepared by recrystallisation and it melts sharply at 140°. The compound Cu_2O, 8PhTh, described in this paper, is also of type (1) in which the copper atom has a co-ordination number of four. The compound 2CuCl, 5PhTh of type (3), obtained in the present work, seems to be a definite compound as various other compounds of this type have been prepared by early workers in different experimental conditions. Compounds 2CuCl, 3Th; 2CuCl, 3AcTh; 2CuCl, 3PhTh of type (8) have been described in the present paper. Compound 2CuCl, 3AcTh has been prepared under two different experimental conditions and hence it may be regarded as a definite compound. The two other compounds, 2CuCl, 3Th and 2CuCl, 3PhTh were also obtained by two analogous methods. The compound 4CuCl, 7AcTh, the only member of type (7), has been obtained by one experimental condition only and therefore it is difficult to judge whether it is a compound or a mixture.

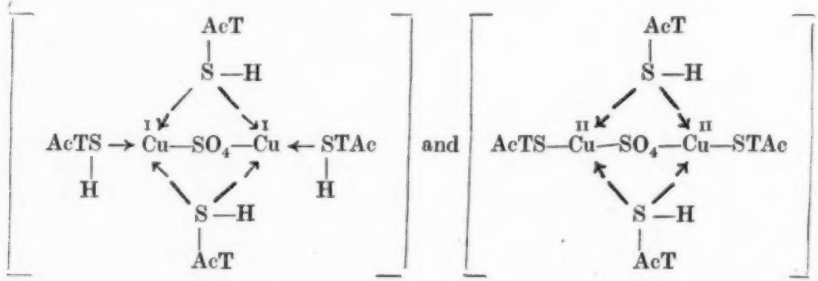
EXPERIMENTAL

Copper Derivatives of N-*Acetylthiourea*

N-*Acetylthiourea* was prepared by the method of Neucki (*Ber.*, 1873, **6**, 599), m.p. 165°. (Found: N, 22.68. $CH_3CONHCSNH_2$ requires N, 23.73%).

Tetrakis-(N-*acetylthiourea*)-*di*-*copper*(I) *Sulphate*.—To an ice-cold solution of *N*-acetylthiourea (10 g.) in aqueous ammonia (1:3; 200 c.c.) was added an ice-cold solution of copper sulphate (5 g. in 50 c.c.) slowly with stirring at a temperature of 0°-10°. The yellow-red precipitate formed was filtered quickly, washed successively with ice-water, cold ethanol, and ether and analysed after air drying. (Found: Cu, 18.28; N, 15.82; total S, 22.81, 22.12, 23.07; SO_4, 13.24. Cu_2SO_4, $4CH_3CONHCSNH_2$ requires Cu, 18.27; N, 16.11; total S, 23.04; SO_4, 13.81%).

The compound is feebly paramagnetic ($\mu_B \approx 0.32$ B.M.), the moment value being abnormally low for copper (II). It seems that the substance is a mixture of the copper (I) compound (A) and copper (II) compound (B), which differ only by two H-atoms and there is but little difference in their analytical compositions.



(A) (B)

(where, AcT stands for $CH_3CONHCNH$)

Arguments in favour of the bridging property of thiourea molecule through the linkage of the S-atom in it to two metal atoms by two co-ordinate bonds have been adduced in Part II of this paper (this *issue*, p. 765).

The substance turns black on slight warming (40°) or on keeping in a vacuum desiccator. It keeps well for nearly one day in air. With HCl (dilute) it turns white with the liberation of H_2S. With NaOH solution it turns black. It is insoluble in water, ethanol, or ether.

Tris-(thiourea)-di-copper(I) *Chloride*.—The preceding substance (5 g.) was rubbed for ½ hour with HCl (1:1; 25 c.c.) in a mortar, cooled in ice, until colour of the substance became milky white; the mixture was then filtered, washed successively with ice-cold water and cold ethanol. It was dried in air and analysed. (Found: Cu, 29.17; N, 19.2; Cl, 17.01. $2CuCl, 3NH_2CSNH_2$ requires Cu, 29.81; N, 19.71; Cl, 16.66%). Analysis shows that the acetyl group in *N*-acetylthiourea has been lost, evidently through hydrolysis caused by the strong hydrochloric acid.

The compound is highly stable and insoluble in HCl. (conc.). With NaOH solution it turns black. It is insoluble in ether, acetone, ethanol, or water and is diamagnetic.

Heptakis-(N-acetylthiourea)-tetra-copper(I) *Chloride*.—Hydrated cupric chloride (1g.) in water (10 c.c.) was added slowly with stirring to a solution of *N*-acetylthiourea (3.5 g.) in 120 c. c. of aqueous acetone (1:4) at the room temperature; the yellowish white precipitate thus formed was filtered and washed successively with water, ethanol, and ether. It was dried in air and analysed. (Found: Cu, 20.87; N, 15.59; Cl, 12. 30. $4CuCl, 7CH_3CONHCSNH_2$ requires Cu, 20.78; N, 16.03; Cl, 11.82%).

The compound is stable and decomposes with NaOH solution, forming a red substance which changes to a black one. It is insoluble in water, ethanol, ether, or acetone and is diamagnetic.

Tris-(N-acetylthiourea)-di-copper (I) *Chloride*.—A solution of anhydrous cupric chloride (1g.) in dry anhydrous acetone (80 c.c.) was added dropwise to a solution of *N*-acetylthiourea (molecular proportion, 1:2; 1.7g) in anhydrous acetone (60 c.c.). A transient red colour appeared which vanished forming a yellow precipitate. The mixture was heated for 5 minutes on a water bath with stirring when the supernatant liquid became colorless. It was then cooled, filtered, and washed with acetone till free of cupric chloride. It was dried in air and analysed. (Found: Cu, 23.24; N, 15.53; Cl, 19.25. $2CuCl, 3CH_3CONHCSNH_2$ requires Cu, 23.00; N, 15.21; Cl, 12.86%).

The same compound was obtained when cupric chloride and *N*-acetylthiourea in molecular proportion (1:1) were used for the preparation.

The compound is stable. With NaOH it turns first red and then black. It is insoluble in water, acetone, or ether and is paramagnetic giving a moment value of 0.26 B.M. It indicates the presence of some copper(II) in the product.

Acid Hydrochloride of Bis-(thiourea)-copper(I) *Chloride*.—To *N*-acetylthiourea (2.5 g.) in 150 c.c. of water was added slowly cuprous chloride (1g., prepared by the method of Daniel, *J. Amer. Chem. Soc.*, 1915, **37**, 1167) in HCl solution (1:1, 4 c.c.), when a white precipitate was formed which was filtered, washed successively with water, ethanol, and ether. It was dried and analysed. (Found : Cu, 21.34; N, 18.93; Cl, 24.20. CuCl, $2NH_2CSNH_2,HCl$ requires Cu, 22.11; N, 19.48; Cl, 24.66%).

The compound is diamagnetic. The acetyl group in *N*-acetylthiourea has evidently been removed by hydrolysis caused by strong hydrochloric acid.

The substance is stable and insoluble in dilute hydrochloric acid. With NaOH it turns black. It is insoluble in water, alcohol, or ether.

Uni-(N-acetylthiourea)-copper Hydroxide.—Copper sulphate (1.75 g.) in water (10 c.c.) was mixed with sodium potassium tartrate (1.75 g.) and NaOH (0.7g.) in 5 c.c. of water and the mixture was cooled in ice. A saturated solution of *N*-acetylthiourea (7g.) in acetone (50 c.c.) at about 0° was added with stirring into the above ice-cold solution, when a red precipitate was formed which was filtered rapidly and washed successively with ice-cold water and cold acetone. It was dried in vacuum at about 10° (without the use of desiccating agent) and analysed. [Found: Cu, 30.80; N, 13.91. (I) $Cu(OH)_2$, $CH_3CONHCSNH_2$ requires Cu, 29.5; N, 12.99; (II) CuOH, $CH_3CONHCSNH_2$, $\frac{1}{2}H_2O$ requires Cu, 30.62; N, 13.51; (III) Cu(-OH)-SC(=NH) $NHCONH_2$, $\frac{1}{2}$ H_2O requires Cu, 30.68; N, 13.54%]. The analytical results rule out formula (1), but cannot decide between formulas (II) and (III).

The compound is stable at ordinary temperature when dry; with NaOH at room temperature it turns red and then black. It is insoluble in water, ethanol, or acetone and is paramagnetic, with a B. M. value of 0.85 per copper atom. The value suggests an admixture of copper (I) and copper (II) compounds of formulas (II) and (III).

Copper Derivatives of S-*Acetylthiourea*

S-Acetylthiourea was prepared by the method of Dixon and Howthorne (*J. Chem. Soc.*, 1907, **97**, 122). [Found: N, 23.29. Calc. for $CH_3COSC(=NH)NH_2$: N, 23.72%]. The substance is deliquescent and its m.p. 109° coincides with that of NH_2-C(=NH)-S-CO-CH_3.HCl, described by Dixon and Howthorne (*loc. cit.*) It is highly soluble and it easily hydrolyses to thiourea and acetic acid. It has comparatively a low solubility in anhydrous acetone or in freshly distilled absolute ethanol, but it is soluble in glacial acetic acid. Its molecular formula has been described by Dixon and Howthorne (*Chem. Zentrl.*, 1907, 1109) to be NH_2-C(=NH)=S-$COCH_3$.HCl, but in our experimental condition (vacuum desiccation) 'HCl' molecule of the substance is gradually lost until at last $H_2N.C(=NH)$-S-$COCH_3$ only remains.

Uni-(S-acetylthiourea)-copper (I) *Chloride.*—When an aqueous solution of cupric chloride (1 g.) was mixed with an aqueous solution of *S*-acetylthiourea, a white spongy precipitate was formed, which was found to be uni-thiourea-copper (I) chloride, described by Rosenheim and Loewenstamm (*Z. anorg. Chem.*, 1903, **24**, 66). Evidently *S*-acetylthiourea hydrolyses with water giving thiourea which forms the complex with copper. The same compound was obtained in slightly aqueous acetone as well. *S*-Acetylthiourea therefore hydrolyses in contact with even a very small amount of water present in the acetone. Use of glacial acetic acid also gave no better results, but formed a mixture of CuCl, $2NH_2CSNH_2$,HCl and CuCl, $2CH_3CONHCSNH_2$, HCl. Finally, a dilute solution of freshly prepared *S*-acetylthiourea in freshly distilled (over silica gel) anhydrous acetone was mixed with a solution of anhydrous cupric chloride (heating $CuCl_2$, $2H_2O$ for 2 hours at 140° in an air oven) in anhydrous acetone, when a white precipitate was formed, which was rapidly filtered, washed with anhydrous acetone, dried at 10° in a desiccator, and analysed after one day. (Found: Cu, 29.63; N, 13.14; Cl, 16.71. $CuCl,CH_3COSC(=NH)$-NH_2

requires Cu, 29.26; N, 12.91; Cl, 16.33%). The compound appears to be fairly stable at room temperature and decomposes near 100° or by alkali solution. It is soluble in water, acetone, or ethanol.

Copper Derivatives of N-*Phenylthiourea*

N-Phenylthiourea was prepared by the method of De Clermont (*Ber.*, 1876, **9**, 446), m. p., 154°. (Found: N, 18.38. Calc. for $C_6H_5NHCSNH_2$: N, 18.40%). It is very little soluble in water, but highly soluble in ether, acetone, or ethanol and is quite stable. Its solubility in water is just a little more than 1% at room temperature (32-33°).

Uni-(*N-phenylthiourea*)*-copper Chloride.*—An ice-cold concentrated solution of anhydrous cupric chloride (2 g.) in absolute ethanol was added slowly with stirring to an ice-cold solution of *N*-phenylthiourea (4.6 g.) in the same medium, when a white precipitate was formed, which was filtered, washed, dried at 10°, and analysed. (Found: Cu, 25.12; N, 11.27; Cl, 14.71. CuCl, $C_6H_5NHCSNH_2$ requires Cu, 25.30; N, 11.15; Cl, 14.14%).

The compound is yellowish white and stable. With NaOH solution it turns black. It is insoluble in ethanol, but soluble in acetone and is paramagnetic, with μ_B (eff.) = 0.64 B.M., which indicates the presence of some copper (II), presumably as the compound Cu(-Cl)-SC(=NH)NHC_6H_5.

Pentakis-(*N-phenylthiourea*)*-di-copper* (I) *Chloride.*—An aqueous solution of cupric chloride hydrate (1 g.) was added with stirring to an aqueous solution of *N*-phenylthiourea (3.5 g.), when a white precipitate was formed. It was filtered, washed successively with water, ethanol, and acetone, and analysed when dry. (Found: Cu, 13.48; N, 15.04; Cl, 7.71; S, 16.55. 2 CuCl, $5C_6H_5NHCSNH_2$ requires Cu, 13.25; N, 14.60; Cl, 7.40; S, 16.70%).

The compound is very stable. An aqueous suspension of the substance does not change in colour even at 100°. With dilute NaOH solution it turns black. It is slightly soluble in water but not in ethanol or acetone. It is diamagnetic.

Hexakis-(*N-phenylthiourea*)*-di-copper*(I) *Sulphate.*—An aqueous solution of copper sulphate (2 g.) was added to an aqueous solution of *N*-phenylthiourea (6 g.) when a white precipitate was formed, which was filtered, washed with water and acetone, dried at 10°, and analysed. (Found: Cu, 10.97; N, 14.57; total S, 18.60, 19.90, 19.84. Cu_2SO_4, $6C_6H_5NHCSNH_2$ requires Cu, 11.2; N, 14.8; total S, 19.73%.)

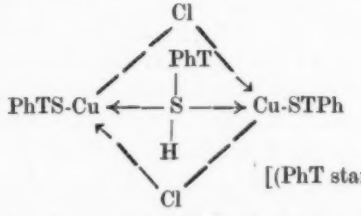
The substance is yellow and stable. Its aqueous suspension on boiling does not change in colour. With NaOH solution in turns black. It is insoluble in water and fairly soluble acetone but highly soluble in ether. It is diamagnetic.

Bis-(*N-phenylthiourea*)*-copper*(I) *Hydroxide.*—Copper sulphate (1 g.) in ice-cold water (25 c.c.) was added slowly to an ice-cold solution of *N*-phenylthiourea (6 g.) in a mixture of 250 c.c. of water, 230 c.c. of liquor ammonia and 20 c.c. of ethanol, when a brown precipitate was formed, which was filtered as usual. (Found: Cu, 16.91; N, 14.62; S, 15.70. CuOH, $2C_6H_5NHCSNH_2$ requires Cu, 16.51; N, 14.56; S, 16.64%). The compound shows a very low magnetic moment [μ_B (eff.) = 0.16 B.M.] indicating presence of some copper (II).

The compound is moderately stable and decomposes by HCl (dil.) or by NaOH (dil.). It is insoluble in water or ethanol but soluble in acetone.

Tris-(*N*-*phenylthiourea*)-*di*-*copper Chloride*.—Bis-(*N*-phenylthiourea)-copper(I) hydroxide, prepared as above, was rubbed in a mortar with hydrochloric acid solution (1:1) when the brown compound was transformed into a white one, which was treated as usual. (Found: Cu, 19.52; N, 12.05; Cl, 11.17. $2CuCl, 3C_6H_5NHCSNH_2$ requires Cu, 19.40; N, 12.84; Cl, 10.87%.)

The compound is highly stable and insoluble in HCl (conc.). It turns black with NaOH solution on boiling. It is insoluble in water, ethanol, or acetone. Is is paramagnetic with μ_B (eff.) = 0.42 B.M., suggesting the presence of some copper (II) in form of the compound shown below.



[(PhT stands for $C_5H_5\dot{N}HC(NH)S$)]

Octakis-(*N*-*phenylthiourea*)-*di*-*copper* (I) *Oxide*.—The preparation of the two compounds $NH_2CSNH_2,Cu(OH)_2$ and $C_6H_5NHCSNH_2,Cu(OH)_2$, described by Dehn (*loc. cit.*), was attempted in the present work following the method of the former; but none of the compounds could be isolated. In the first case, a grass-green precipitate, claimed by Dehn to be $NH_2CSNH_2,Cu(OH)_2$, was formed at 0°, but during filtration at room temperature of about 30°, it turned black, being changed to insoluble copper sulphide. In an attempt to prepare the yellow compound, $C_6H_5NHCSNH_2,Cu(OH)_2$, a solution containing 1.75g. of Rochelle salt, 0.7g. of sodium hydroxide in 5 c.c. water, and 1.75 g. of copper sulphate in 10 c. c. of water was added to an ice-cold, saturated solution of *N*-phenylthiourea in acetone, when a beautiful green compound containing no nitrogen or sulphur was obtained. In a subsequent attempt an excess of ice-cold water was added to the well-cooled mixture of "Fehling solution" and acetone solution of *N*-phenylthiourea, when a yellow compound was precipitated, which was filtered, washed with ice-cold water, dried in a vacuum desiccator at 10°, and analysed. (Found: Cu, 9.42; N, 17.4; S, 18.95. $Cu_2O, 8C_6H_5NHCSNH_2$ requires Cu, 9.35; N, 16.50; S, 18.86%).

The compound is moderately stable. With NaOH solution it turns black on boiling. It is insoluble in water, but soluble in acetone or ether. The corrected value of the atomic susceptibility for Cu has been found to be $+ 4.7 \times 10^{-6}$ at 31°; the feeble paramagnetism might be due to impurities. The magnetic susceptibilities of most of the compounds obtained were measured by a Gouy balance in a maximum field strength of 9.36×10^3 gauss and a current strength of 5 amperes. The values of μ_B (eff.) have been calculated by applying the air correction and the diamagnetic correction.

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Search for New Antispasmodics. Part X

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The Mannich bases (V and VI) have been obtained. The base (VI) forms the isonitroso derivative (VII), which has been reduced to the amine (VIII).

A current hypothesis (Lands and Luduena, *J. Pharmacol. Exptl. Therap.*, 1956, **117**, 331) of antimuscarine action is that acetylcholine-sensitive receptor surfaces of parasympathetically innervated organs, can be effectively blocked by a compound which has two foci for attachment to the surface. One of these foci is a terminal tertiary or quaternary nitrogen atom and the other, which must be between 5 and 10 Å distant from the nitrogen head, may be one of a number of as yet ill-defined groupings to which is attached one or more groups large enough to constitute, like an umbrella, a protective shield over the receptors and to prevent access to them of the natural neurohormone. By considering the structure of the active antispasmodics it appears that the unshared electrons of a polarised carbonyl or ethylene group, or the lone pair on a hydroxyl oxygen, or a second nitrogen atom constitutes the second focus for attachment to the receptor surface (Goldberg and Wragg, *J. Chem. Soc.*, 1957, 4823).

An approach, based on the above hypothesis, would be to incorporate large groups in the appropriate position of a chain having two active foci, one of which is a terminal tertiary nitrogen atom ; this led to the synthesis (Ghosh, Bose, and Raychaudhuri, this *Journal*, 1959, **36**, 319) of 4-phenyl-4-benzyl-1-piperidinobutan-3-one (I) and of 4-phenyl-4-benzyl-2-amino-1-piperidinobutan-3-one (II). These compounds, which incorporate large groups like phenyl and benzyl in the appropriate position of a chain having two active foci, have been subjected to preliminary testing in this laboratory by Dr. A. N. Bose and Shri S. Bose for antispasmodic activity. Whereas the compound (I) can neutralise the contractions due to 1 μg. of carbachol in a concentration of 10^{-6}, (II) is active even in a concentration of 10^{-8}. The compound (I) is active in neutralising histamine in a concentration of 5×10^{-6}, but (II) is active under similar conditions in a concentration of 10^{-8}. This antihistaminic activity can be attributed to the presence of an ethylamine skeleton (cf. Idson, *Chem. Rev.*, 1950, **47**, 307). Both the compounds show neutralisation of barium chloride (500 μg.) stimulation of the gut at a dose level varying between 20 μg. and 100 μg. Thus these compounds show appreciable antispasmodic activity, combining both neurotropic and musculotropic action and also exerting some activity against histamine-induced spasm. The compound (II), however, lacks the requisite property of tissue binding, which is necessary for sustained action. Its *N*-acetyl derivative, on the other hand, shows an improved tissue binding while retaining the same range of activity.

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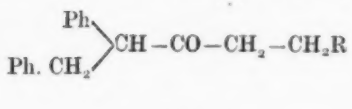
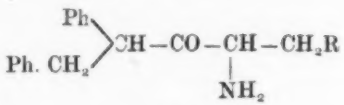


(I)

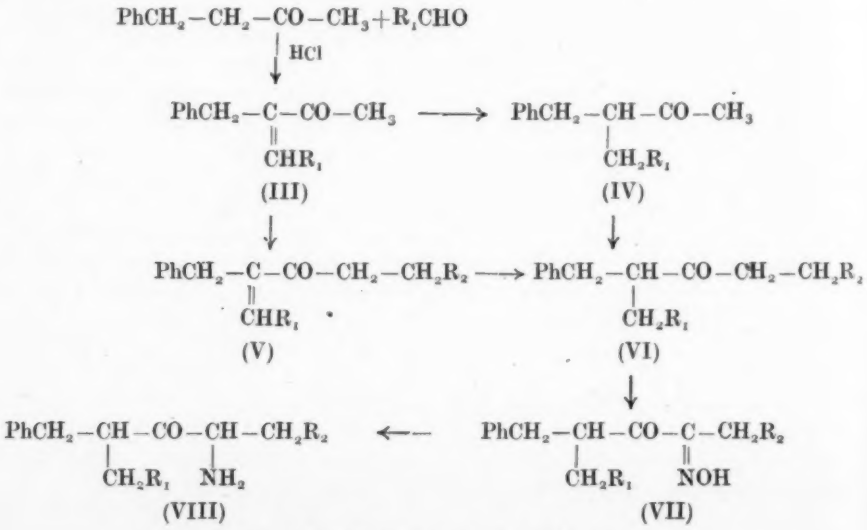


(II)

(R=piperidino)

The above observations are of sufficient interest to warrant extension of the above line of investigation and it has been considered desirable to synthesise compounds of the types (I) and (II) with differently constituted large groups (e.g., two benzyl groups) attached to the same active focus. It has been observed that under acid-catalysed condition, the condensation of an aromatic aldehyde with unsymmetrical ketones, like methyl ethyl ketone, phenylacetone, etc., takes place at the methylene carbon atom, whereas under base-catalysed condition the methyl group is involved (Goldschmidt and Krczmar, *Monatsh.*, 1897, **18,** 437; 1898, **19,** 406; 1901, **22,** 657; Harries and Müller, *Ber.*, 1902, **35,** 966). Benzylacetone has now been condensed with benzaldehyde in presence of an acid catalyst and the product has been assigned the structure 1-phenyl-2-benzylidene-butan-3-one (III: R_1=Ph), further confirmed by the observation that on catalytic hydrogenation (III: R_1=Ph) yields 1,1-dibenzylacetone (IV: R_1=Ph). When subjected to the Mannich reaction with paraformaldehyde and piperidine, compound (III) furnishes the aminoketone (V), which has been catalytically hydrogenated over Pd—C to yield (VI). It is significant to observe that the compound (IV), on the Mannich reaction, yields (VI) and this lends further support to the postulate that methyl group is more reactive than methynyl for the Mannich reaction (cf. Ghosh, Bose, and Raychaudhuri, this *Journal*, 1960, **37,** 93).

With butyl^n nitrite the base (VI) forms the isonitroso derivative, which, on hydrogenation over palladium-charcoal, furnishes the amino compound (VIII), isolated as hydrochloride.



[R_1=Ph or $C_6H_4.OCH_3$ (*p*); R_2=piperidino]

EXPERIMENTAL

1-*Phenyl*-2-*benzylidenebutan*-3-*one* (III : R_1=Ph).—Benzaldehyde (12.8 g.) was dropwise added under stirring to a solution of benzylacetone (14.8 g.) in ethanolic hydrochloric acid (15 c. c.) and the mixture was stirred for 6 hours. The reaction mixture was taken up in ether and washed free of acid. The solution was dried (sodium sulphate) and the ether removed. After a forerun of benzylacetone and benzaldehyde, a colorless viscous liquid (10 g., b.p. 190-200°/3-4 mm) was collected. On chilling it solidified. It was crystallised from petroleum ether (b.p. 40-60°) in colorless needles, m.p. 72-73°. (Found: C, 86.52; H, 6.60. $C_{17}H_{16}O$ requires C, 86.44; H, 6.78%). The *semicarbazone* was crystallised from ethanol in colorless needles, m.p. 184-85°. (Found : N, 14.54. $C_{18}H_{19}ON_3$ requires N, 14.33%). The *2,4-dinitrophenylhydrazone* was crystallised from ethanol in red needles, m.p. 190-91°.

Palladium-charcoal (10%, 0.2 g.) was added to a solution of the above compound (III: R=Ph; 6 g.) in ethanol (75 c. c.) and the mixture was shaken at room temperature with hydrogen at atmospheric pressure when one equivalent of hydrogen was gradually absorbed and further absorption of hydrogen practically stopped. The solution was filtered and distilled to remove ethanol. The residue was distilled at 182-87°/10 mm to furnish a thick liquid (IV: R_1=Ph; 6 g.). Vavon and Conia (*Compt. rend.*, 1946, **222**, 245) reported b.p. 192-94°/15 mm. The *semicarbazone* was crystallised from ethanol in colorless needles, m.p. 153-54°. (Found: N, 14.59. $C_{18}H_{21}ON_3$ requires N, 14.24%). The *oxime* was crystallised from ethanol in colorless needles, m.p. 76°. (Found: N, 5.38. Calc. for $C_{17}H_{19}ON$: N, 5.53%). Vavon and Conia (*loc. cit.*) reported m.p. 75°. The *2,4-dinitrophenylhydrazone* was crystallised from ethanol in golden needles, m.p. 123-24°. (Found: N, 13.55. Calc. for $C_{23}H_{22}O_4N_4$: N, 13.40%). Barnes and Beitchman (*J. Amer. Chem. Soc.*, 1954, **76**, 5430) reported m.p. 126-27°.

1-*Phenyl*-2-(p-*methoxy*)-*benzylidenebutan*-3-*one* [III: R_1=C_6H_4 OCH_3 (*p*)] was similarly prepared by treating benzylacetone (14.8 g.) with anisaldehyde (16.3 g.) in presence of ethanolic hydrochloric acid (15 c. c.) and was obtained as a faintly coloured, thick liquid (14 g.; b. p. 230-40°/20-25 mm). On chilling it solidified and was crystallised from petroleum ether (b. p. 60-80°) in colorless plates, m.p. 79-80°. (Found: C, 80.84; H, 6.68. $C_{18}H_{18}O_2$ requires C, 81.20; H, 6.77%). The *semicarbazone* was crystallised from ethanol in colorless needles, m.p. 194°. (Found: N, 13.34. $C_{19}H_{21}O_2N_3$ requires N, 13.00%). The *2,4-dinitrophenylhydrazone* was crystallised from ethanol in red needles, m.p. 191°. (Found: N, 12.73. $C_{24}H_{22}O_5N_4$ requires N, 12.56%).

1-*Phenyl*-2-*benzylidene*-5-*piperidinopentan*-3-*one* (V : R_1=Ph; R_2=piperidino).—A mixture of (III : R_1=Ph; 5.9 g.), piperidine hydrochloride (5 g.), paraformaldehyde (1.2 g.), HCl (conc., 0.15 c.c.), and ethanol (40 c.c.) was heated under reflux on the steam-bath for 12 hours. Ethanol was distilled and the residue (hydrochloride) was filtered, washed with ether, and crystallised from ethanol in colorless needles, m.p. 187°. (Found: C, 74.92; H, 7.74. $C_{23}H_{27}ON$, HCl requires C, 74.70; H, 7.58%). The *oxalate* was crystallised from ethanol in colorless rectangular plates, m.p. 172°. [Found: N, 3.75. $C_{23}H_{27}ON.(CO_2H)_2$ requires N, 3.31%].

1-*Phenyl*-2-(p-*methoxy*)-*benzylidene*-5-*piperidinopentan*-3-*one* [V: R_1=C_6H_4-OCH_3 (*p*); R_2=piperidino] was similarly prepared as hydrochloride, which crystallised from ethanol in colorless plates, m.p. 165°. The *picrate* was crystallised from benzene-ethanol mixture in yellow needles, m.p. 174°. (Found: N, 9.80. $C_{24}H_{29}O_2N.C_6H_3O_7N_3$ requires N, 9.46%).

The *oxalate* was crystallised from ethanol in colorless plates, m.p. 194-95°. [Found; N, 3.33. $C_{24}H_{29}O_2N.(CO_2H)_2$ requires N, 3.09%].

1-*Phenyl*-2-*benzyl*-5-*piperidinopentan*-3-*one* (VI: R_1=Ph: R_2=piperidino). — Palladium-charcoal (10%; 0.2 g.) was added to a solution of the hydrochloride of (V: R_1=Ph; R_2=piperidino; 6 g.) in ethanol (175 c.c.) and the mixture was shaken at room temperature with hydrogen at atmospheric pressure, when one equivalent of hydrogen was gradually absorbed and further absorption of hydrogen practically stopped. The catalyst was removed by filtration and washed with ethanol. The filtrate and washings were combined and removal of ethanol left a viscous liquid which was purified by acid-ammonia treatment. The *hydrochloride* was prepared and was crystallised from ethanol in colorless needles, m.p. 154°. (Found: C, 74.48; H, 7.62. $C_{23}H_{29}ON$,HCl requires C, 74.29; H, 8.07%). The *oxalate* was crystallised from ethanol in colorless rectangular plates, m. p. 145-46°. [Found: N, 3.42. $C_{23}H_{29}ON.(CO_2H)_2$ requires N, 3.29%].

The above hydrochloride was obtained when (IV: R_1=Ph) was allowed to react with piperidine hydrochloride and paraformaldehyde in the usual way.

1-*Phenyl*-2-*benzyl*-4-*oximino*-5-*piperidinopentan*-3-*one* (VII: R_1=Ph; R_2=piperidino).—Butyl^n nitrite (3 g.) was added to a cooled suspension of hydrochloride of (VI: R_1=Ph; R_2=piperidino; 3.6 g.) in anhydrous ether (40 c. c.). Dry hydrochloric acid gas was passed till saturation, when a deep red-coloured solution was obtained. After keeping overnight in the cold, the mixture was poured in ice and the solution was shaken with ether. The aqueous solution was basified with ammonia when a solid (2.5 g.) was obtained. It was crystallised from aqueous ethanol in colorless needles, m.p. 100-101°. (Found: N, 7.99. $C_{23}H_{28}O_2N_2$ requires N, 7.69%).

1-*Phenyl*-2-*benzyl*-4-*amino*-5-*piperidinopentan*-3-*one* (VIII: R_1=Ph; R_2=piperidino).—Palladium-charcoal (10%; 0.1 g.) was added to a solution of (VII: R_1=Ph; R_2=piperidino; 2.5 g.) in ethanol (200 c. c.) and the mixture was shaken at room temperature in an atmosphere of hydrogen. When an equivalent quantity of hydrogen was absorbed, the catalyst was filtered and the filtrate was made acidic to Congo red by passing dry hydrochloric acid gas. The solvent was then removed and the residue was crystallised from ethanol-ether mixture in colorless needles, m.p. 160-62°. (Found: C, 71.78; H, 8.41; N, 7.55. $C_{23}H_{30}ON_2$, HCl requires C, 71.41; H. 8.02; N, 7.24%).

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Compounds of Tungsten(VI) Oxytetrachloride with Nitroanilines, Aminobenzoic Acids, Aminophenols, Ketones, Amides, and Anilides

Sarju Prasad and K. S. R. Krishnaiah

Compounds of tungsten(VI) oxytetrachloride with nitroanilines, aminobenzoic acids, aminophenols, ketones, amides, and anilides have been prepared, their properties studied, and structures discussed.

In earlier communications (this *Journal*, 1961, **38**, 352) the action of tungsten (VI) oxytetrachloride on some amines and heterocyclic bases and that of WCl_6 with aminophenols, aminobenzoic acids, nitroanilines, amides, and anilides (this *Journal*, 1961, **38**, 177) have been reported. The work has now been extended to study the preparation and properties of compounds of $WOCl_4$ with nitroanilines, aminobenzoic acids, aminophenols, ketones, amides, and anilides.

EXPERIMENTAL

Tungsten(VI) oxytetrachloride was prepared, as reported earlier, and extracted with CS_2. The organic solvents were dehydrated and distilled. The other chemicals used were of B. D. H. or E. Merck's 'extra pure' quality.

In all the cases, except urea and benzanilide, a moderately strong solution of the base in benzene was slowly added to the solution of $WOCl_4$ in CS_2 with constant shaking till the precipitation was complete and the base was in slight excess. In the case of urea and benzanilide, the compound was prepared by adding an excess of $WOCl_4$ in CS_2 to a suspension of these in benzene and the mixture left for 48 hrs. in a dry atmosphere with frequent shaking. It was filtered, the precipitate washed with benzene till free of the base, and dried in a vacuum desiccator at the room temperature. Tungsten, chlorine, and nitrogen were estimated as described earlier.

General Properties.—The compounds are coloured, fairly stable in dry atmosphere, and insoluble in benzene and ether but sparingly soluble in CS_2, EtOH, and acetone. These begin to hydrolyse when brought in contact with water and are decomposed by acids and alkalies.

DISCUSSION

An examination of the results (Table I) shows that four molecules of nitroanilines and aminobenzoic acids combine with one molecule of $WOCl_4$ and the compounds formed are similar to those obtained with aromatic amines (*loc. cit.*). The nitro and carboxyl groups do not co-ordinate in presence of a strong donor group like $-NH_2$.

TABLE I

	Organic compound.	Compound formed.	Colour.	%Tungsten.		%Chlorine.		% Nitrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
1.	o-Nitroaniline	$[WO(NO_2.C_6H_4NH_2)_4]Cl_4$	Dark brown	20.67	20.58	15.47	15.86	-	-
2.	m- ,, ,,	Do	Light brown	20.43	20.58	15.78	15.86	-	-
3.	p- ,, ,,	Do	Greyish brown	20.81	20.58	15.80	15.86	-	-
4.	o-Aminobenzoic acid	$[WO(COOH.C_6H_4NH_2]_4)Cl_4$	Light pink	20.40	20.67	15.71	15.93	-	-
5.	p-Aminobenzoic acid	Do	Light blue	20.51	20.67	16.04	15.93	6.23	6.30
6.	o-Aminophenol	$[WO(OH.C_6H_4NH_2)_2]Cl_4$	Brown	32.69	32.86	25.10	25.33	4.84	5.00
7.	m- ,, ,,	Do	Dirty green	33.13	32.86	25.26	25.33	:	-
8.	p- ,, ,,	Do	Light green	32.90	32.86	25.48	25.33	-	-
9.	Acetophenone	$[WO(C_6H_5.CO.CH_3)_4]Cl_4$	Blue	22.33	22.39	17.14	17.26	-	-
10.	Benzophenone	$[WO(C_6H_5CO.C_6H_5)_4]Cl_4$	Ash	17.16	17.20	13.16	13.25	-	-
11.	Michler's ketone	$[WO\{(CH_3)_2.N.C_6H_4.CO.C_6H_4.N(CH_3)_2\}_4]Cl_4$	Dirty yellow	13.33	13.00	9.93	10.02	-	-
12.	Urea	$[WO\{CO(NH_2)_2\}_4]Cl_4$	Grey	31.87	31.61	24.09	24.37	18.79	19.25
13.	Acetamide	$[WO(CH_3CONH_2)_4]Cl_4$	Dirty grey	32.03	31.84	24.52	24.54	-	-
14.	Benzamide	$[WO(C_6H_5CONH_2)_4]Cl_4$	Blue	22.14	22.27	17.10	17.17	-	-
15.	Acetanilide	$[WO(CH_3.CO.NH.C_6H_5)_4]Cl_4$	Light blue	20.78	20.85	16.17	16.08	6.32	6.25
16.	p-Aminoacetanilide	$[WO(CH_3.CO.NH.C_6H_4NH_2)_4]Cl_4$	Light blue	19.50	19.53	14.84	15.05	12.08	11.90
17.	Benzanilide	$[WO(C_6H_5.CO.NH.C_6H_5)_4]Cl_4$	Greenish grey	16.48	16.29	12.30	12.55	-	-

In the case of aminophenols only two molecules of these combine with one molecule of $WOCl_4$, showing thereby the co-ordination of both $-NH_2$ and hydroxyl groups. The compounds are fairly stable, probably due to the formation of chelate compounds.

In the case of ketones, amides, and anilides four molecules of each combine with one molecule of $WOCl_4$ and the compounds are considerably stable. The carbonyl group present in these molecules being very reactive and also the affinity of tungsten towards oxygen being strong, it appears that chlorine is readily displaced to the outer ring and the compound obtained with urea may be represented as $[WO\{CO(NH_2)_2\}_4]Cl_4$. Similar results were obtained in the formation of compounds of WCl_6 with amides and anilides (*loc. cit.*).

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Amino Derivatives of Tungsten(VI) Oxytetrachloride. Part II

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The amino derivatives of tungsten(VI) oxytetrachloride have been prepared by the action of tungsten(VI) oxytetrachloride on some aromatic secondary and tertiary amines, and heterocyclic bases; their properties have been studied and structures discussed.

No attempt appears to have been made to study the reactions of $WOCl_4$ with secondary and tertiary amines and heterocyclic bases in organic solvents. Von Beck (*Z. anorg. allgem. Chem.*, 1931, **196**, 85) prepared some complex bromotungstites like pyridinium tetrabromotungstite $(C_5H_5NH)WOBr_4$, tetraethylammonium tetrabromoaquotungstite $(C_2H_5)_4N\,[WOBr_4(H_2O)]$, etc. In an earlier communication the preparation and properties of the compounds of $WOCl_4$ with some aromatic primary mono-and diamines have been reported (this *Journal*, 1961, **38**, 352) and the work is now extended to study the action of $WOCl_4$ on some secondary and tertiary amines and heterocyclic bases.

EXPERIMENTAL

Tungsten (VI) oxytetrachloride was prepared as described in Part I (*loc. cit.*). The organic solvents were dehydrated and distilled. The amines and other chemicals used were of B. D. H. or E. Merck's 'extra pure' quality.

The compounds were prepared by adding slowly a solution of the amine in benzene to $WOCl_4$ in CS_2 with constant shaking till the amine was in slight excess. In the case of secondary amines, the compounds formed settled down immediately, but with tertiary amines and heterocyclic bases, the compounds separated after shaking the mixture for a long time. The precipitate was filtered and washed with benzene till free of the amine. All the operations were carried out in a dry atmosphere and the products were finally dried over calcium chloride in a vacuum desiccator.

Tungsten, chlorine, and nitrogen were estimated as in Part I (*loc. cit.*).

TABLE I

Compounds of tungsten(VI) oxytetrachloride with heterocyclic bases.

	Heterocyclic base.	Compound formed.	Colour.	%Tungsten.		% Chlorine.	
				Found.	Calc.	Found.	Calc.
1.	Pyridine	$[WO(C_5H_6N)_4]Cl_4$	Brown	27.53	27.96	21.37	21.55
2.	Piperidine	$[WO(C_5H_{11}N)_4]Cl_4$	Reddish brown	27.06	26.99	20.64	20.80
3.	α Picoline	$[WO(C_6H_7N)_4]Cl_4$	Brown	25.64	25.77	19.42	19.86
4.	γ-Picoline	Do	Light brown	25.73	25.77	19.78	19.86
5.	Quinoline	$[WO(C_9H_7N)_4]Cl_4$	Chocolate brown	21.30	21.44	16.18	16.53
6.	Piperazine	$[WO(C_4H_{10}N_2)_2]Cl_4$	Light pink	35.53	35.80	27.53	27.60
7.	2-Aminopyridine	$[WO(NH_2.C_5H_4N)_2]Cl_4$	Yellowish brown	34.19	34.71	26.40	26.76

TABLE II

Compounds of tungsten (VI) *Oxytetrachloride with secondary and tertiary amines.*

	Amine.	Compound formed.	Colour.	% Tungsten. Found.	% Tungsten. Calc.	% Chlorine. Found.	% Chlorine. Calc.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	Methylaniline	$[WO(C_6H_5NH.CH_3)_4]Cl_4$	Light brown	24.07	23.90	18.21	18.42	..	..
2.	Ethylaniline	$[WO(C_6H_5NH.C_2H_5)_4]Cl_4$	Ash	22.23	22.27	17.04	17.17	..	..
3.	Benzylaniline	$[WO(C_6H_5NH.CH_2C_6H_5)_4]Cl_4$	Brown	17.40	17.13	12.97	13.20	..	..
4.	Diphenylamine	$[WO(C_6H_5NH.C_6H_5)_4]Cl_4$	Black	18.12	18.07	13.69	13.93	5.39	5.50
5.	Diphenylbenzidine	$[WO\{(C_6H_4.NH.C_6H_5)_2\}_2Cl_4$	Light dirty green	18.40	18.14	13.47	13.98	..	..
6.	Dimethyl-*p*-phenylene diamine	$[WO\{C_6H_4(NH.CH_3)_2\}_2]Cl_4$	Violet	29.82	29.96	22.72	23.10	9.05	9.12
7.	Dimethylaniline	$[WO\{C_6H_5N(CH_3)_2\}_4]Cl_4$	Ash	22.13	22.27	17.43	17.17	6.54	6.78
8.	Diethylaniline	$[WO\{C_6H_5N(C_2H_5)_2\}_4]Cl_4$	Grey	19.67	19.62	15.07	15.12	..	..
9.	Dibenzylaniline	$WO[C_6H_5N(CH_2C_6H_5)_2]_2Cl_4$	Brown	20.48	20.72	15.83	15.97	3.09	3.16
10.	*p*-Aminodimethylaniline	$[WO(Me_2N.C_6H_4.NH_2)_2]Cl_4$	Dark brown	29.71	29.96	23.29	23.10	9.04	9.12
11.	*p*-Aminodiethylaniline	$[WO(Et_2N.C_6H_4NH_2)_2]Cl_4$	Black	28.03	27.46	20.72	21.16	..	..

DISCUSSION

The compounds formed with tungsten(VI) oxytetrachloride and aromatic secondary and tertiary amines and heterocyclic bases are similar to those formed with aromatic primary amines. These are insoluble in benzene and ether but sparingly soluble in CS_2, ethanol, and acetone. The compounds are considerably stable in dry atmosphere, but when exposed to moist air they absorb moisture and decompose. Those obtained with tertiary amines and heterocyclic bases are very hygroscopic. These are decomposed by acids and alkalies.

On heating alone, the compounds afford a sublimate which is soluble in water, is acidic, and responds to the test for Cl and the corresponding organic base. When heated with sodalime, the corresponding amine or heterocyclic base separates out.

The compounds formed with dimethyl-*p*-phenylenediamine, diphenylbenzidine, *p*-aminodimethylaniline, *p*-aminodiethylaniline, 2-aminopyridine, and piperazine are considerably stable, due to the formation of chelate compounds.

The structures of these compounds appear to be similar to those formed with primary amines as shown in Part I (*loc. cit.*).

It is interesting to note that only two molecules of dibenzylaniline combine with one molecule of $WOCl_4$, which is probably due to steric hindrance.

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Reactions of Tungsten(VI) Oxytetrachloride with Organic Acids

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Preparation and properties of the compounds formed by the interaction of tungsten(VI) oxytetrachloride with some organic acids have been studied and their structures discussed.

A general survey of the literature shows that some salts of tungsten have been prepared (this *Journal*, 1961, **38**, 153) by the action of WCl_6 on some organic acids, but no work appears to have been done to prepare similar salts of $WOCl_4$ with organic acids. The present investigation was therefore undertaken with a view to studying the preparation and properties of compounds of $WOCl_4$ with some organic acids.

EXPERIMENTAL

Tungsten (VI) oxytetrachloride was prepared by the method described earlier (this *issue*, p. 760). The organic solvents were dehydrated and distilled. The other chemicals used were of B. D. H. or E. Merck's 'extra pure' quality.

Low-melting acids in benzene were added in excess to $WOCl_4$ in CS_2 and refluxed on a water bath till the evolution of HCl had ceased. In the case of other acids these solvents were evaporated in an oil bath, the temperature of which was then raised 10-20° above the m.p. of the respective acid, and the heating continued till the evolution of HCl had ceased. The products obtained were repeatedly washed with benzene or other organic solvents till free of the acid and dried in a vacuum desiccator.

Tungsten was estimated as WO_3 and the organic matter was found by difference. Carbon and hydrogen were estimated in a few cases by the combustion method.

All the compounds are coloured, very stable in dry atmosphere, and do not respond to the test for chlorine. These are insoluble in common organic solvents but sparingly soluble in ethanol. The compounds formed with lauric, myristic, palmitic, and stearic acids are, however, sparingly soluble in benzene and hydrolyse slowly on boiling with water; these are decomposed by acids and alkalies.

It is evident that one molecule of $WOCl_4$ reacts with four molecules of monocarboxylic and two molecules of dicarboxylic acids, the reaction being more vigorous with the latter and is completed in a comparatively short time. The hydroxy-acids react vigorously with $WOCl_4$ and the hydrogen of both the carboxyl and hydroxyl groups is displaced. Nitrocarboxylic acids give similar compounds to those obtained with carboxylic acids and hydroxy-acids. In all the cases the corresponding tungsten salts are formed.

The author's sincere thanks are due to the authorities of the Banaras Hindu University for providing the necessary facilities.

TABLE I

	Acids.	Compound formed.	Colour.	% Tungsten.		%Carbon.		%Hydrogen.	
				Found.	Calc.	Found.	Calc.	Found.	Calc.
1.	Lauric	$WO[CH_3(CH_2)_{10}COO]_4$	Ash	18.53	18.47	..	..	..	..
2.	Myristic	$WO[CH_3(CH_2)_{12}COO]_4$	,,	16.91	16.61	..	..	..	..
3.	Palmitic	$WO[CH_3(CH_2)_{14}COO]_4$	Greyish brown	14.94	15.98	..	..	..	..
4.	Stearic	$WO[CH_3(CH_2)_{16}COO]_4$	Brown	14.09	13.80	..	..	..	..
5.	Benzoic	$WO[C_6H_5COO]_4$	,,	26.80	26.89	48.36	49.13	2.81	2.29
6.	Crotonic	$WO[CH_3CH=CH.COO]_4$	Deep brown	34.30	34.06	..	..	..	..
7.	Cinnamic	$WO[C_6H_5CH=CHCOO]_4$	Brown	22.93	23.34	..	..	..	..
8.	*o*-Nitrobenzoic	$WO[NO_2.C_6H_4COO]_4$	Light brown	20.84	21.28	..	..	..	..
9.	*p*-Nitrobenzoic	Do	Brown	21.16	21.28	..	..	..	..
10.	Malonic	$WO[CH_2(COO)_2]_2$	Brownish black	45.64	45.53	..	..	..	..
11.	Adipic	$WO[(CH_2)_4(COO)_2]_2$	Black	37.09	37.79	..	..	..	..
12.	Phthalic	$WO[C_6H_4(COO)_2]_2$	Brownish black	35.63	34.84	..	..	..	..
13.	Succinic	$WO\left[\begin{matrix}CH_2COO\\ CH_2COO\end{matrix}\right]_2$	Brown	41.87	42.58	20.97	22.23	1.798	1.852
14.	Camphoric	$WO[C_8H_4(COO)_2]_2$	Greyish brown	26.19	26.42	..	..	..	..
15.	Salicylic	$WO\left[C_6H_4\begin{matrix}O\\ COO\end{matrix}\right]_2$	Brown	38.30	38.97	35.07	35.60	1.624	1.695
16.	3,5-Dinitrosalicylic	$WO\left[(NO_2)_2.C_6H_2\begin{matrix}O\\ COO\end{matrix}\right]_2$	Light brown	28.18	28.21	..	..	..	..

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Complex Compounds of Substituted Thioureas. Part II. Mercury(II) Derivatives of *N*-Acetylthiourea

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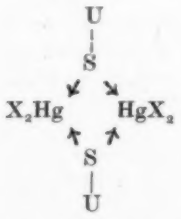
With mercuric chloride and *N*-acetylthiourea, two compounds, mono- and bis-(*N*-acetylthiourea)-mercuric chlorides, have been obtained, whereas with mercuric iodide, only one such compound, the mono-(*N*-acetylthiourea) complex has been isolated. The constitution of these compounds has been discussed.

Five different types of thiourea complexes with mercuric ion have been described so far in the literature (cf. Beilstein's Handbuch), namely, those containing (*a*) four, (*b*) three, (*c*) two, (*d*) one, and (*e*) two-third molecules of thiourea, respectively, per mercuric ion. The complex compounds of substituted thiourea with mercuric ion have not so far been reported excepting $3HgCl_2$, 2 etus (etus represents ethylenethiourea), described by Hofmann (*Ber.*, 1873, **6**, 598). It has now been found that *N*-acetylthiourea forms with mercuric chloride and mercuric iodide only complexes of the type (*c*), viz., $HgCl_2$. 2AcTh, and two others are of the type (*d*), viz., $HgCl_2$. AcTh and HgI_2. AcTh (AcTh represents *N*-acetylthiourea). The tendency for co-ordination of thiourea with mercuric ion seems to decrease in *N*-acetylthiourea.

Tetraco-ordination of the meruric ion confers a stable radon structure to it and in conformity with this idea the tetra-, tri-, bis-, and mono-thiourea-mercuric complexes can be represented by (I) (II), (III), and (IV) respectively.

$[Hg\text{-}(SU)_4]X_2$ (I) $\quad [SO_4\text{-}Hg\text{-}(SU)_3]$ (II) $\quad [X_2\text{-}Hg\text{-}(SU)_2]$ (III)



(IV)

[S-U represents $S\text{—}C\langle^{NHR}_{NHR}$. X = monovalent acid radical. R = R′ = H atom or alkyl, aryl, or other organic radicals.]

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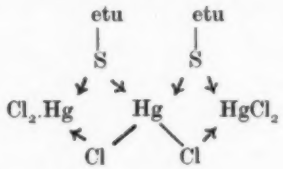
The mercuric tetrathiourea chloride is soluble in water and hence has been represented as a salt as in (I), whereas all the compounds of tri-, bis-, and mono-thiourea types, described previously as also in the present paper, are fairly insoluble in water but soluble in organic solvents. Hence these have been represented to be non-electrolytes as in (II), (III), and (IV) respectively. The mono-thiourea-mercuric salts, represented as in (IV), are binuclear compounds with thiourea molecules serving as bridges.

With other metals thiourea complexes are known to be formed containing fractional molecules of thiourea per metal atom. Morgan and Burstall (*J. Chem. Soc.*, 1928, 143) suggest that the $-NH_2$ groups of thiourea molecule may also take part in the co-ordination, thus enabling thiourea molecule to bridge two metal atoms. The present authors suggest that with the help of two lone pair of electrons, the S-atom of thiourea forms two co-ordination bonds with two different metal atoms, thus forming a bridge between them; the S-atom in such a thiourea bridge will become tetra-covalent. The bridging property of thiourea molecule is presumably manifested in the compound, $3HgCl_2$, 2Setu (etu represents $C.N_2H_2C_2H_4$) described by Hofmann (*loc. cit.*) as shown in (V).



(V)

EXPERIMENTAL

All the reagents used were of analytical quality. *N*-Acetylthiourea was prepared by the method of Neucki (this *issue*, p. 647).

Mono-(N-acetylthiourea)-mercuric Chloride.—To a nearly ice-cold, saturated solution of *N*-acetylthiourea (1.2 g.) in anhydrous acetone (10 c. c.) was added a nearly saturated ice-old solution of mercuric chloride (3 g.) in anhydrous acetone (10 c. c.). On keeping the mixture in a refrigerator for sometime, a white solid crystallised out, which was washed with ice-cold acetone solution (1:1) and then once with ice-cold anhydrous acetone. It was dried in air and analysed. (Found: N, 6.81; Cl, 17.33; Hg, 50.1. $HgCl_2$, $CH_3CONHCSNH_2$ requires N, 6.88; Cl,17.4; Hg, 49.3%).

The substance is stable but with NaOH it decomposes forming mercuric sulphide. It is insoluble in water but fairly soluble in acetone.

Bis-(N-acetylthiourea)-mercuric Chloride.—A nearly saturated solution of mercuric chloride (1.4 g.) in acetone solution (1:1) was added slowly with stirring to a concentrated solution of *N*-acetylthiourea (2.4 g.) in the same solvent (mol. proportion 1:4). The white spongy precipitate thus formed was washed successively with acetone and ethanol. It was dried in air and analysed. (Found: N, 11.54; Cl, 14.33; Hg, 39.90. $HgCl_2$, $2CH_3CONHCSNH_2$ requires N,11.08; Cl, 14.02; Hg, 39.68%).

The same substance was obtained by taking mercuric chloride and *N*-acetylthiourea in the molecular proportion of 1:8 (in aqueous acetone medium), and 1:4 (in anhydrous acetone medium) and hence complexes containing more than two molecules of *N*-acetylthiourea per molecule of mercuric chloride probably do not exist. It resembles the previous compound in properties.

Mono-(N-acetylthiourea)-mercuric iodide was prepared from mercuric iodide (1 mole) and *N*-acetylthiourea (1 mole) in cold acetone solution. The mixture was kept at 0° for sometime and then on dilution with excess of ice-cold water, a white precipitate was formed which changed to yellow. It was filtered, washed with water, dried, and analysed. (Found: N, 5.00; I, 44.45; Hg, 35.59. $HgI_2,CH_3CONHCSNH_2$ requires N, 4.89; I, 44.34; Hg, 35.04%).

The same compound was obtained even by using an excess of *N*-acetylthiourea (1:2). Its properties resemble those of the corresponding chloro compound.

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Organic Pesticides. Part VI. Synthesis of Certain Fluorophenols and their Allyl Ethers

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For studying pesticidal activity of organic fluorine compounds, six fluorophenols have been prepared by the Clemmensen reduction of the corresponding fluorohydroxyketones, reported earlier. All of them have been converted into their allyl ethers. These twelve compounds have been evaluated for their insecticidal activity with adult house flies (*Musea domestica*) as the test insect.

Phenols have wide antimicrobial activity and the halogen atom and the alkyl groups, when attached to the aromatic nucleus, enhance greatly this toxicity (Gruenhagen *et al.*, Contributions from Boyce Thomson Institute, 1951, **16**, 349). Very little work appears to have been done on arylphenols containing fluorine (Kindler *et al.*, *Chem. Ber.*, 1953, **86**, 501; 1954, **87**, 194). We have now prepared six fluoro-alkyl and-aryl substituted phenols as potential pesticides by the Clemmensen reduction of certain fluorohydroxyketones reported earlier (Joshi and Bahel, this *Journal*, 1960, **37**, 687).

Further, phenolic ethers have also been investigated as pesticides (Felton and McLaughlin, *J. Org. Chem.*, 1947, **12**, 298). The validity of the hypothesis that a good contact insecticide must have a combination of a toxic and lipoid-soluble groupings in its molecule (Lauger *et al.*, *Helv. Chim. Acta*, 1944, **27**, 918) was justified by Lauger *et al.* who also showed that allyloxy-aryl ethers possessed a marked toxicity. We have therefore converted the above fluorophenols into their allyl ethers so that the compounds contain both a neurotoxic halo-aryl group and an ether linkage having lipophilic property.

The insecticidal activity of these compounds has been evaluated against adult house flies (*Musea domestica*) and some of them have been found to be fairly active.

EXPERIMENTAL

Fluorohydroxyketones were prepared by the method reported in an earlier communication (*loc. cit.*). Fluorophenols were obtained by the Clemmensen reduction of the above hydroxyketones.

Amalgamated zinc was prepared by shaking for 15 minutes a mixture of zinc (20 g.), mercuric chloride (20 g.), HCl (conc., 20 c.c.), and water (10 c. c.), decanting, and finally washing the residue with water. It was refluxed with ethanol (30 c.c.), HCl (conc., 10 c.c), and the fluorohydroxyketone (0.02*M*) for 10 to 12 hours, during which 2 c. c. portion of HCl (conc.) was added after every hour. At the end of this period a drop of the liquid failed to give any colour with aqueous ferric chloride solution. After removal of ethanol the residue was extracted with ether. The ethereal layer was washed successively with 2%

TABLE I

TABLE I

Fluorophenols.

*S. No.	Hydroxyfluoroketones.	Alkyl or aryl fluorophenols.	Yield.	B.P	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	R-*o*-chlorophenyl-K	2-(*o*-Chloro-)-benzyl-Fp	41.7%	245°/10 mm	$C_{13}H_{10}OClF$	65.56	65.53	4.23	4.39
2.	R-*p*-fluorophenyl-K	2-(*p*-fluoro)-benzyl-Fp	95.8	270°/15	$C_{13}H_{10}OF_2$	70.63	70.90	4.34	4.54
3.	R-*m*-tolyl-K	2-(*m*-Methyl)-benzyl-Fp	83.4	**260°/3	$C_{14}H_{13}OF$	77.55	77.77	5.84	6.01
4.	R-*p*-methoxyphenyl-K	2-(*p*-Methoxy)-benzyl-Fp	88.7	185°/7	$C_{14}H_{13}O_2F$	72.12	72.41	5.55	5.60
5.	R-Heptyl^n-K	2-Octyl^n -Fp	73.0	200°/30	$C_{14}H_{21}OF$	74.76	75.00	9.23	9.39
6.	R-styryl-K	2-(1′-Phenyl)-propenyl-Fp	83.5	235°/16	$C_{15}H_{13}OF$	79.05	79.44	5.74	5.70

* These index-numbers have been used in Table III.

** Melts completely at 155°.

R= 1-hydroxy-4-fluorophenyl.

K= ketone (2-acyl).

Fp= 4-fluorophenol.

TABLE II

****Allyl (alkyl or aryl) ethers.**

*S. N.	Allyl-Ethers	Yield.	B.P.	Formula.	%Carbon. Found.	%Carbon. Calc	% Hydrogen. Found.	% Hydrogen. Calc.
7.	A-2-(*o*-chloro-)benzyl-Fb	42.5%	190°/2mm	$C_{16}H_{14}OClF$	69.76	69.43	5.20	5.06
8.	A-2-(*p*-fluoro-)-benzyl-Fb	63.5	195°/30	$C_{16}H_{14}OF_2$	73.61	73.84	5.20	5.38
9.	A-2-(*m*-methyl-)-benzyl-Fb	67.7	200°/2	$C_{17}H_{17}OF$	78.92	79.25	6.34	6.64
10.	A-2-(*p*-methoxy-)benzyl-Fb	85.1	140°/4	$C_{17}H_{17}O_2F$	74.69	75.00	6.38	6.25
11.	A-2-octyl^n-Fb	84.6	150°/2	$C_{17}H_{25}OF$	76.96	77.27	9.21	9.41
12.	A-2-(1′-phenyl)propenyl-Fb	68.2	170°/2	$C_{18}H_{17}OF$	80.09	80.59	6.21	6.34

**Six Fluorophenols used are the same as in Table I.

*These index-numbers have been used in Table III.

A= 1-allyloxy.

Fb= 4-fluorobenzene.

sodium carbonate solution and water and dried over anhydrous calcium chloride; the ether was removed and the residue distilled under reduced pressure. The compounds are listed in Table I.

Allyl Ethers.—These were prepared by the method reported earlier (*loc. cit.*) by treating the phenol (0.1 *M*) with allyl bromide (0. 11 *M*) and freshly fused potassium carbonate (0.15 *M*) in dry acetone (100 c. c.) medium. The allyl ethers obtained are listed in Table II.

Evaluation of Insecticidal Activity.—The insecticidal activity was evaluated against adult house flies (*Musea domestica*) as the test insect. The compounds were dissolved in acetone and later diluted in kerosine oil. The samples were first tested at a concentration of 1%, adopting the usual glass plate petri dish method. The results of these tests, however, did not prove quite successful as the mean mortality did not reach 100% even at the end of 24 hours of exposure. Subsequent trials, using the various materials as space sprays in specially constructed metallic chambers, also proved inconclusive. Finally, the technique of applying the products at high concentration on the basis of mg. of active ingredient per square foot on glass slabs was again adopted. The results of these tests are summarised in Table III.

TABLE III

Formulation.	Dosage. (mg./ft^2.)	Replications.	Mean K. D. time. 50%(M.S.)	100% (H.M.S.)
Sample No. 1	201.60	10	28.04	1.18.00
Sample No. 2	232.65	10	58.07	Overnight
Sample No. 3	225.90	10	11.47	,,
Sample No. 4	166.95	7	3.22	6.44
Sample No. 5	45.00	10	11.33	19.32
Sample No. 6	208.80	10	14.58	34.18
Sample No. 7	193.50	10	19.30	36.04
Sample No. 8	164.25	10	40.20	2[illegible].03
Sample No. 9	45.00	10	3.50	6.20
Sample No. 10	45.00	10	3.08	5.27
Sample No. 11	45.00	10	10.17	18.31
Sample No. 12	190.00	10	26.00	43.56

The samples No. 4, 9, and 10 have been found to be most promising, whereas others are mildly effective as insecticides. The samples may prove insecticidally efficient for a different range of insects, but due to limited facilities at our disposal, these could not be investigated over a greater spectrum.

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Preparation and Study of Hydroxytriazenes as Analytical Reagents. Part III. 3-Hydroxy-1-*p*-tolyl-3-methyltriazene as a Reagent for Palladium and Copper

H. K. L. Gupta and N. C. Sogani

3-Hydroxy-1-*p*-tolyl-3-methyltriazene is found to be a highly selective reagent for the gravimetric determination of palladium and copper and for their separation from a large number of elements by direct weighing in the *p*H range from 1.0 to 6.0 and 3.2 to 6.0 respectively. The reagent offers a positive advantage over other hydroxytriazenes as it is fairly soluble in hot water and excess of it used during the precipitation of the complex can be easily washed. A comparative study of the reactions of 3-hydroxy-1-*p*-tolyl-3-phenyltriazene and 3-hydroxy-1-*p*-tolyl-3-methyltriazene has been made.

In Part II of this series (Gupta, Jain, and Sogani, this *Journal*, 1960, **37**, 531) 3-hydroxy-1-*p*-tolyl-3-phenyltriazene has been reported as a highly selective reagent for gravimetric determination of palladium and copper. In the present communication 3-hydroxy-1-*p*-tolyl-3-methyltriazene has been described as an analytical reagent for the same purpose. This compound possesses identical chelating system to the compounds described earlier in Part I (Sogani and Bhattacharyya, *ibid.*, 1959, **36**, 563) and Part II (*loc. cit.*) with the difference that the oxime group is attached to a methyl group in place of a phenyl group. The characteristic complex forming properties are generally retained though precipitating property is lessened. This compound has a great advantage over other hydroxytriazenes in being fairly soluble in hot water and any excess of the reagent used during the precipitation can easily be removed by washing the complex with hot water.

A study of the reactions of the reagent with various ions shows that at low *p*H it reacts only with palladium, copper, vanadium, iron, molybdate, and vanadate. The complexes given by former two elements are stable towards heat in acidic medium. Selectivity can be increased by using proper masking agents and also by carrying out the determinations between *p*H 1.2 and 3.0 in case of palladium and 3.3 and 4.0 in case of copper.

EXPERIMENTAL

The reagent was prepared by the method described earlier (Gupta and Sogani, this *Journal*, 1959, **36**, 87). It was crystallised from 75% ethanol in the form of yellowish white needles, m.p. 110-11° (lit. m.p. 115-16°, Elkins and Hunter, *J. Chem. Soc.*, 1938, 1346). (Found: N, 25.62. $C_8H_{11}ON_3$ requires N, 25.45%). It is freely soluble in ethanol. Its solubility in water at 34° is 0.0308 g./100g. water and at 75° is 0.0905 g./100g. water.

Reactions with Various Elements.—The reactions were carried out by adopting the conventional procedures. Completeness of the precipitation was tested by applying the spot test on the filtrate. Details of the reactions of 3-hydroxy-1-*p*-tolyl-3-phenyltriazene

and 3-hydroxy-1-*p*-tolyl-3-methyltriazene towards various elements are recorded in Table I. The reactions of other phenylhydroxylamine derivatives are similar to the former and those of methylhydroxylamine derivatives are similar to the latter.

TABLE I

Comparative study of the reactions.

[Q=quantitative. N.Q.=Not quantitative. N.R.=No reaction.]

Elements.	3-Hydroxy-1-*p*-tolyl-3-phenyltriazene.	3-Hydroxy-1-*p*-tolyl-3-methyltriazene.
Fe^{2+}	*p*H 4.9 to 7.0, bluish black granular ppt., unstable towards heat; Q	N.R.
Fe^{3+}	Do	Below *p*H 2, blue colour; above *p*H 4, violet blue ppt.; N.Q.; masked by fluoride.
Cu^{2+}	*p*H 2.0 to 7.0, chocolate-brown granular ppt. stable towards heat; Q.	*p*H 3.2 to 7.0, reddish brown granular ppt. stable towards heat; Q.
Ni^{2+}	*p*H 4.4 to 7.0, bright yellow granular ppt. stable towards heat; Q.	Above *p*H 6.5, yellowish brown ppt. N. Q.; below *p*H 5, N. R.
Pd^{2+}	*p*H 1.6 to 7.0, yellowish brown granular ppt. stable towards heat; Q.	*p*H 1.0 to 6.0, violet brown granular ppt. stable towards heat; Q.
Mn^{2+}	Above *p*H 5.5, dirty brown ppt. unstable towards heat; N. Q.	N.R.
Cd^{2+}	Above *p*H 6.0, light yellow fine ppt.; N.Q.	N.R.
Ti^{4+}	*p*H 2.0 to 3.5, orange ppt. unstable towards heat; Q.	N.R.
Ce^{4+}	N.R.	Below *p*H 2, light yellow colour.
V^{4+}	Below *p*H 2.5, grassy green ppt. unstable towards heat.	Below *p*H 2, brown ppt. unstable towards heat; masked by fluoride.
Vanadate	Below *p*H 2.5, dark green ppt. unstable towards heat.	Below *p*H 2.5, unstable green solution; becomes turbid on keeping
Molybdate	Below *p*H 3.0, deep orange ppt. usntable towards heat	Below *p*H 2.0, yellow ppt.; becomes brown on keeping; N.Q; masked by fluoride.
Ag^{+}, Au^{3+}	Reduced to metallic state.	Reduced to metallic state.

The phenylhydroxylamine derivatives develop an intense yellow colour in alkaline medium and hydrolyse on heating in weakly acidic medium. The hydrolysed products give blue colour in alkaline medium (Part I, *loc. cit.*) The methylhydroxylamine derivatives do not give such reactions.

1% Reagent solution (w/v) in 50% ethanol was used. Other solutions and instruments etc. were the same as described in Part II (*loc. cit.*).

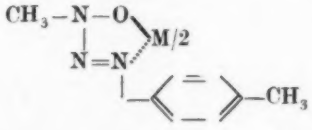
Conditions for Quantitative Precipitation.—Determinations, made by using varying amounts of the reagent and under different *p*H conditions, show that palladium is completely precipitated between *p*H 1.0 and 6.0 by using double the required quantity of

the reagent and copper between *p*H 3.2 and 6.0 by using more than 2½ times the required quantity of the reagent. To increase the selectivity of the reagent, *p*H between 1.2 and 3.0 and between 3.3 and 4.0 were used for palladium and copper respectively.

As^{3+}, Sb^{3+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Be^{2+}, Th^{4+}, U^{4+}, UO_2^{2+}, Zr^{4+}, tungstate, phosphate, borate, fluoride, alkali, and alkaline earth metals give no reaction with either of the reagents.

Properties of the Complexes.—Palladium complex is violet brown in colour and granular in nature. It is insoluble in ethanol, methanol, and ether and is fairly soluble in chloroform and benzene. It was crystallised from benzene in the form of fine crystals, m.p. 239°. It does not show any sign of decomposition before melting and can safely be heated to 120-30° to a constant weight in about half an hour. [Found: N, 9.82. $(C_8H_{10}ON_3)_2Pd$ requires N, 9.63%].

Copper complex is reddish brown in colour. It is slightly soluble in ethanol, fairly soluble in acetone and ether, and freely soluble in chloroform and benzene. It is completely insoluble in 20% ethanol which can be used for washing the precipitate. It was crystallised from ethanol as reddish brown, shining crystals, m.p. 186°. It does not decompose before melting and can be dried to a constant weight between 110° and 120° in about half an hour. [Found: N, 10.56. $(C_8H_{10}ON_3)_2Cu$ requires N, 10.72%]. The chelate can be represented as



(where M=Pd or Cu).

Procedure for Palladium.—Standard palladium solution containing 5 to 30 mg. of the metal was taken in a 400 c.c. beaker and to this were added 10% HCl (v/v; 5 c.c.) and 10% sodium acetate solution (w/v; 3 to 4 c. c.) so that *p*H of the solution after dilution was about 1.5 (*p*H can also be adjusted by using mineral acid alone). The solution was diluted to about 200 c. c. and heated over a water bath. To the hot solution, which may also contain varying amounts of foreign ions, an excess of 1% w/v reagent solution was added with constant stirring. For every mg. of palladium precipitated, 1 c.c. of 1% reagent solution was used. The palladium complex separates out as a violet-brown precipitate. The suspension was heated for about 40 minutes over a water bath during which period the complex became granular and the solution clear. The complex was then filtered hot through a sintered glass crucible No. 3 and washed with hot water 3 to 4 times till the filtrate gave no bluish violet colour with ferric chloride solution. It was then dried to a constant weight at 110-20° for about half an hour and weighed. The weight of the complex multiplied by 0.2454 gave the weight of palladium. The results are recorded in Table II.

Fe^{2+} does not react with the reagent, but during the course of precipitation some of it is invariably oxidised to the ferric state and gives blue colour with a slight turbidity. Zirconium salts are hydrolysed. The interference due to these and also due to vanadium and molybdate was eliminated by using fluoride (10 c.c. of 5% sodium fluoride solution). The interference due to hydrolysis of bismuth and antimony was avoided by using sodium potassium tartrate. Hydrolysis of cerium was checked by adding small amounts of solid ammonium sulphate.

Separation of Palladium from Platinum.—Qualitative reactions of the reagent indicate that it gives no reaction with platinum. But on heating on a water bath, platinum chloride was partially reduced to the metal by the reagent and higher results were obtained. The procedure was therefore slightly modified. To the solution of palladium containing platinum, after the adjustment of *p*H and dilution etc., the reagent solution was added in cold with constant stirring and filtered after about an hour. After two initial washings with cold water to remove any platinum left, it was washed with hot water to remove the excess of the reagent. It was then processed as usual. The results are recorded in Table II.

TABLE II

Pd taken.	Foreign ion.	Pd complex.	Pd found.	Error.
6 mg.	-	0.0242 g.	5.94 mg.	−0.06 mg.
18	-	0.0735	18.03	+0.03
24	-	0.0978	24.00	±0.00
18	Ni^{2+},0.1 g.	0.0733	17.99	−0.01
18	Co^{2+},0.1	0.0735	18.03	+0.03
18	Zn^{2+},0.1	0.0732	17.96	−0.04
18	Cd^{2+},0.1	0.0733	17.99	−0.01
18	Mn^{2+},0.1	0.0736	18.06	+0.06
18	Fe^{2+},0.1	0.0734	18.01	+0.01
18	Fe^{3+},0.1	0.0736	18.06	+0.06
18	Zr^{4+},0.1	0.0734	18.01	+0.01
18	V^{4+},0.1	0.0732	17.96	−0.04
18	Bi^{3+},0.1	0.0735	18.03	+0.03
18	Sb^{3+},0.1	0.0736	18.06	+0.06
18	Ce^{4+},0.1	0.0733	17.99	−0.01
18	Cr^{3+},0.1	0.0736	18.06	+0.06
18	Be^{2+},0.1	0.0734	18.01	+0.01
18	Th^{4+},0.1	0.0735	18.03	+0.03
18	Hg^{2+},01	0.0737	18.08	+0.08
18	As^{3+},0.1	0.0736	18.06	+0.06
18	UO^{2+},0.1	0.0735	18.03	+0.03
18	Molybdate,0.1	0.0733	17.99	−0.01
18	Tungstate, 0.1	0.0733	17.99	−0.01
12	Pt^{4+},0.05	0.0490	12.02	+0.02
12	Pt^{4+},0.1	0.0492	12.07	+0.07
12	Pt^{4+},0.15	0.0491	12.05	+0.05

Procedure for Copper.—Standard copper sulphate solution containing 10 to 30 mg. of copper was taken in a 100 c.c. beaker and after adjusting the *p*H to about 2.40, 1% reagent solution(0.7 c.c.) was added for every mg. of copper present. When sodium potassium tartrate is used as a buffering agent, amount of the reagent is 1.5 c.c. of 1% solution for every mg. of copper. Rest of the procedure is the same as described in the case of palladium. The weight of the complex multiplied by 0.1623 furnishes the weight of copper. The results are recorded in Table III.

DISCUSSION

3-Hydroxy-1-*p*-tolyl-3-methyltriazene has a distinct advantage over 3-hydroxy-1,3-diphenyltriazene (Sogani and Bhattacharyya, *Anal. Chem.*, 1956, **28**, 81, 1616) and 3-hydroxy-1-*p*-tolyl-3-phenyltriazene (*loc. cit.*) which have been claimed to be superior

to the conventional reagents employed for the gravimetric determination of palladium as it is fairly soluble in hot water and excess of it used during precipitation can easily be removed by washing with hot water. Moreover, it affords a simple method for the separation of palladium from platinum. The reagent is not however, specific for copper as the working *p*H is slightly higher at which other elements interfere.

TABLE III

Cu taken.	Foreign ion.	Cu complex.	Cu found.	Eerror.
10 mg	-	0.0618 g.	10.03 mg.	+0.03 mg.
20	-	0.1232	19.99	—0.01
30	-	0.1853	30.07	+0.07
10	Co^{2+},0.1 g.	0.0619	10.05	+0.05
10	Ni^{2+},0.1	0.0615	9.97	—0.03
10	Zn^{2+},0.1	0.0618	10.03	+0.03
10	Mn^{2+},0.1	0.0620	10.07	+0.07
10	Cd^{2+},0.1	0.0615	9.97	—0.03
10	Hg^{2+},0.1	0.0619	10.05	+0.05
10	Fe^{2+},0.1	0.0615	9.97	—0.03
10	Fe^{3+},0.1	0.0618	10.03	+0.03
10	Cr^{3+},0.1	0.0618	10.03	+0.03
10	Al^{3+},0.1	0.0620	10.07	+0.07
10	Bi^{3+},0.1	0.0619	10.05	+0.05
10	Sb^{3+}0.1	0.0620	10.07	+0.07
10	Molybdate 0.1	0.0617	10.01	+0.01

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Diazoketones from Salicyl and Cinnamoyl Chlorides

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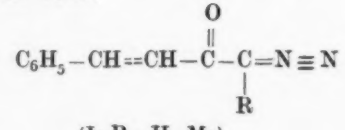
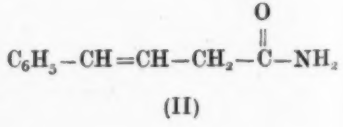
1-Diazo-4-phenyl-3-butenone and 1-diazo-1-methyl-4-phenyl-3-butenone have been prepared from cinnamoyl chloride (1 mol.) and diazomethane (2.5 mols.) and diazoethane (2.5 mols.) respectively. Salicyl chloride (1 mol.) with diazomethane [2.5 mols. and 4 mols. (excess)] gives a mixture of ω-diazo-o-hydroxyacetophenone and ω-diazo-o-methoxyacetophenone. All these diazoketones have been identified.

Acid chlorides like salicyl and cinnamoyl chlorides contain two sites of reactivity towards diazomethane. By using different amounts of diazomethane [4 mols. (excess) and 2.5 mols.] per molecule of cinnamoyl chloride, several workers (Wotiz and Buco, *J. Org. Chem.*, 1955, **20,** 210; Grundmann and Frischmann, *Annalen*, 1945 **524,** 31; Moore, *J. Org. Chem.*, 1955, **20,** 1607) obtained a mixture containing 4-phenyl-5-diazoacetylpyrazoline and 1-diazo-4-phenyl-3-butenone in different amounts. The diazoketones so obtained have been subjected to some of their well-known reactions (Moore, *loc. cit.*; Wotiz and Buco, *loc. cit.*). We prepared 1-diazo-4-phenyl-3-butenone (I:R=H) and 1-diazo-1-methyl-4-phenyl-3-butenone (I:R=Me) from cinnamoyl chloride (1*M*) and diazomethane and diazoethane (2.5*M*) respectively in ether solution at 0°.

Although the ketone (I:R=H) has been described (Wotiz and Buco, *loc. cit.*; Moore, *loc. cit.*) we found that our sample, after crystallisation twice from ethanol, melted at 177° (Wotiz and Buco, *loc. cit.*, report m. p. 173°). Moreover, we could accomplish the Arndt and Eistert synthesis (*Ber.*, 1935, **68,** 204) with ammonia using Ag_2O as a catalyst and obtained an amide (II), m.p. 129° (Kohl, *Ber.*, 1903, **36,** 174, reports m.p. 130°), which involved Wolff's rearrangement (*Annalen*, 1912, **394.,** 40). The compound (I:R=H) on treatment with ethanolic KOH (Yates and Shapiro, *J. Amer. Chem. Soc.*, 1959, **81,** 212) gave cinnamic acid and ammonia, indicating the presence of a double bond.

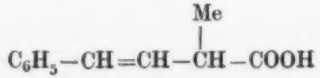


(I: R=H, Me)



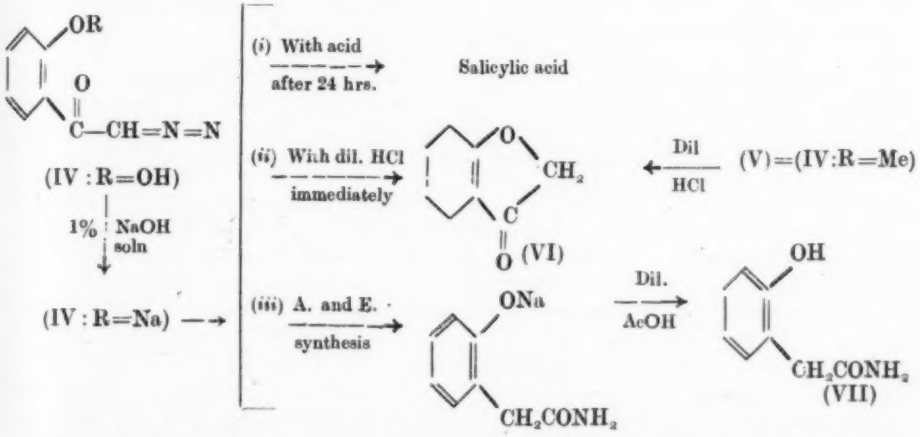
(II)

The diazoketone (I:R=Me) on crystallisation from ethanol melted at 170°. When subjected to the Arndt and Eistert synthesis, it gave ∝-methyl-γ-phenylvinylacetic acid (III), m.p. 109° (Fittig and Liebmann, *Annalen*, 1882, **255**, 262, report m.p. 110.5°). Treatment of (I:R=Me) with ethanolic KOH gave cinnamic acid (Yates and Shapiro, *loc. cit.*).



(III)

2-Hydroxy-3-naphthoyl chloride on treatment with diazomethane affords 2-hydroxy-3-naphthoyldiazomethane (Krzikalla and Eistert, *J. prakt. Chem.*, 1935, *ii*, **143**, 50). Thus in the formation of this diazoketone, methylation of phenolic group does not take place. We found, however, that salicyl chloride (1*M*) on treatment with diazomethane (2.5*M* and 4*M*) respectively gave a mixture of ω-diazo-*o*-hydroxyacetophenone (IV) and ω-diazo-*o*-methoxyacetophenone (V). The formation of the mixture of the diazoketones (IV) and (V) is quite similar to that of the mixture of 1-diazo-4-phenyl-3-butenone and 4-phenyl-5-diazoacetylpyrazoline (*loc. cit.*). Thus the phenolic group was methylated in both the cases, but the amount of the latter was found to be more than that of the former when 4 mols. of diazomethane were used. The ether solution containing the diazoketones after keeping overnight gave a violet coloration with ferric chloride, indicating the presence of a phenolic group. The solution was concentrated by removing some solvent. When 4 mols. of diazomethane were used, the excess of diazomethane distilled with ether. The ether solution was treated with 1% NaOH solution, when ω-diazo-*o*-hydroxyacetophenone dissolved in aqueous layer as its sodium compound. The aqueous layer was divided into three portions. One portion was kept for 24 hours, which on acidification gave salicylic acid, m. p. 158° (Yates and Shapiro, *loc. cit.*), thus proving the presence of a phenolic group in the diazoketone (IV). The second portion was immediately just acidified with HCl (dil.) and extracted with ether. The ether extract gave coumaranone (VI), m. p. 104° (Bose and Yates, *J. Amer. Chem. Soc.*, 1952, **74**, 4703). The formation of coumaranone can be explained by the mechanism described by Bose and Yates (*loc. cit.*). The third portion of the aqueous layer was subjected to the Arndt and Eistert synthesis (*loc. cit.*), when the sodium compound of *o*-hydroxyphenylacetamide (VII) was obtained, from which it was isolated on acidification with dilute acetic acid, m. p. 116° (Stoermer, *Annalen*, 1900, **313**, 86, reports m.p. 116-17°). The amide on hydrolysis gave *o*-hydroxyphenylacetic acid (VIII), m. p. 137° (Pschorr *et al.*, *Ber.*, 1900, **33**, 166, report m. p. 137°).



The above reactions completely establish the identity of ω-diazo-*o*-hydroxyacetophenone (IV).

The ether solution left after treatment with 1% NaOH did not give any coloration with ferric chloride. On removal of the ether a liquid was obtained, a portion of which on treatment with dilute HCl gave coumaranone (VI), m. p. 104° (Bose and Yates, *loc. cit.*).

The other portion, when subjected to the Arndt and Eistert synthesis, gave, as expected, *o*-methoxyphenylacetamide (IX), m.p. 131° (Seth and Deshapande, this *Journal*, 1950, **27**, 429, report m.p. 131°.). This confirmed the identity of ω-diazo-*o*-methoxyacetophenone.

The formation of some ω-diazo-*o*-methoxyacetophenone from 2.5 mols. of diazomethane is as expected. But the existence of ω-diazo-*o*-hydroxyacetophenone, even when 4 mols. of diazomethane are used, is noteworthy.

EXPERIMENTAL

Diazoketones (I: R=H; R=Me) were prepared from cinnamoyl chloride (1 mol., 8.5 g.) and diazomethane and diazoethane (each 2.5 mols., 5.5 g. and 7.0 g. respectively) in ether solution at 0°. The diazoketones were thrown out on evaporation of some of the solvent.

1-*Diazo*-4-*phenyl*-3-*butenone* (I: R=H) was crystallised twice from ethanol, m.p. 177°. (Found: C, 69.1; H, 5.28; N, 15.9. $C_{10}H_8ON_2$ requires C, 69.7; H, 4.6; N, 16.2%).

It gave with ammonia and $AgNO_3$ β-benzylidenepropionamide. It crystallised from hot water, m.p. 129°.

The diazoketone (I: R=H), when treated with aqueous ethanolic KOH, gave cinnamic acid, m.p. 133°. A mixed melting point showed no depression.

1-*Diazo*-1-*methyl*-4-*phenyl*-3-*butenone* (I: R=Me) was crystallised from ethanol, m.p. 170°. (Found: C, 70.2; H, 4.9; N, 14.6. $C_{11}H_{10}ON_2$ requires C, 70.9; H, 53.; N, 15.05%).

When subjected to the Arndt and Eistert synthesis, it gave α-methyl-γ-phenylvinylacetic acid, crystallised from hot water, m.p. 109°. (Found: Equiv., 175.5. $C_{11}H_{12}O_2$ requires equiv., 176).

The diazoketone (I: R=Me), when treated with aqueous ethanolic KOH, gave cinnamic acid, m.p. 133° (undepressed by mixed m.p.).

ω-Diazo-o-hydroxyacetophenone (IV) *and ω-Diazo-o-methoxyacetophenone* (V).—Salicyl chloride (1 mol., 6.4g.) was treated with diazomethane (2.5 mols., 4.4g. and 4 mols., 6.8 g. respectively) at 0°. The ether solutions were concentrated by distillation and extracted with 1% NaOH solution. Both aqueous and ethereal layers were treated with the results described earlier (*vide supra*).

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Oximidobenzotetronic Acid: A New Reagent for the Spectrophotometric Determination of Cobalt

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An ethanolic solution of oximidobenzotetronic acid reacts with an aqueous solution of cobalt to form a deep red, water-soluble complex above *p*H 10.0. The complex is quite stable and obeys Lambert-Beer's law at 485 mμ within the concentration range of 0 to 4.7 p.p.m. of cobalt and quantities as small as 0.02 p.p.m. of the metal can be estimated spectrophotometrically. Interference due to certain foreign ions has been studied. The most probable chelate structure, based on the evidence obtained from infrared spectrum of the compound, has been proposed.

Among many of the organic reagents reported for the colorimetric and spectrophotometric determination of cobalt, Sandell ("Colorimetric Determinations of Traces of Metals", 2nd ed., p. 271, Interscience Publishers Inc., 1950) has described and recommended nitroso-R-salt (sodium 1-nitroso-2-hydroxynaphthalene-3, 6-disulphonate), *o*-nitrosophenol, and *o*-nitrosocresol. Thiocyanate method has been extensively used. William (*Talanta*, 1958, **1**, 88) has recently surveyed the various organic reagents recommended for the colorimetric and absorptiometric determination of cobalt. Some new reagents that have been more recently suggested are : isonitroso (oximino) dimedone (Bossche and Hoste, *Anal. Chim. Acta*, 1958, **18**, 564), quinolinedione dioxime (Golvovina *et al.*, *Vestn. Moskov. Unic.*, 1957, **5**, 187), pyridine thiocyanate (Forsythe *et al.*, *Talanta*, 1958, **1**, 249), *N*-oximinoacetylanthranilic acid (Buscaróns and Munné, *Anal. Chim. Acta*, 1958, **19**, 432), sodium *p*-(mercaptoacetamido)benzene sulphonate (Gupta and Sogani, *Anal. Chem.*, 1959, **31**, 918), *NN'*-ethylenedi-(4-methoxy-1,2-benzoquinone-1-oxime-2-imine) (Mashima, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80**, 1263), nicotinamidoxime (Tripathi and Banerjee, *Z. anal. Chem.*, 1959, **168**, 407). and dithio-oxamide (Jacobs and Yoe, *Anal. Chim. Acta*, 1959, **20**, 332). There are various disadvantages in the use of the above reagents as many cations and anions cause interference and in most cases organic solvents are needed either to keep the complex in solution or for its extraction.

We have found that oximidobenzotetronic acid can be successfully employed for the spectrophotometric determination of cobalt. The reagent has already been used by Bhat and Jain (unpublished) for the spectrophotometric determination of Fe^{2+}. When a freshly prepared ethanolic solution of oximidobenzotetronic acid is added to an aqueous solution of cobalt, a brownish red suspension is produced, which dissolves completely in excess of alkali to form a deep red complex instantaneously. This reaction has been utilised for the estimation of cobalt in quantities as small as 0.02 p.p.m. of the metal in solution. The red complex so produced is water-soluble and is not extractable by organic solvents like benzene, chloroform, ether, and pentanol[n]. The complex is quite stable for more than a week and the optical density of the complex is unaffected at the temperature range of 5°-to 50°. The colour intensity is maximum and remains unchanged above *p*H 10.0. The

complex obeys Lambert-Beer's law at 485 mμ within the concentration range of 0 to 4.7 p.p.m. of cobalt. The estimation of cobalt with this reagent can be carried out even in presence of large amounts of the usually interfering foreign ions.

EXPERIMENTAL

4-Hydroxycoumarin was prepared by the method of Stahman *et al.* (*J. Amer. Chem. Soc.*, 1943, **65**, 2285) and readily converted into oximidobenzotetronic acid by nitrous acid as described by Anschütz *et al.* (*Annalen*, 1909, **367**, 169). Ethanolic solutions of the reagent were used.

$CoSO_4, 7H_2O$ (A. R.-B.D.H) was used for making standard solutions of cobalt. The stock solution was 2.01×10^{-3} *M* and 10 c.c. of it on dilution to 500 c. c. had a concentration of 4.7 p.p.m. of cobalt. All other reagents employed were of either A.R. (B.D.H) or *Pro Analysi* (Merck) quality.

A Unicam spectrophotometer, model SP 600, was used for all spectrophotometric studies. The thickness of the absorption cells used was 10 mm. All *p*H measurements were taken on a Beckman *p*H meter, model H2.

The ultraviolet absorption spectrum of oximidobenzotetronic acid has already been reported. (Bhat and Jain, *loc. cit.*). The absorption spectra of cobalt-oximidobenzotetronic acid was taken at various dilutions of cobalt between the *p*H range 10.0 and 12.5. The complex exihibited maximum absorption at 485 mμ as shown in Fig. 1. The

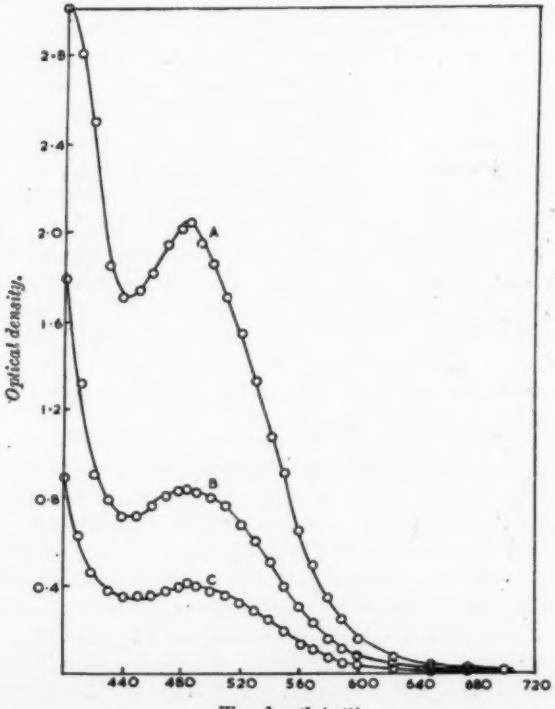
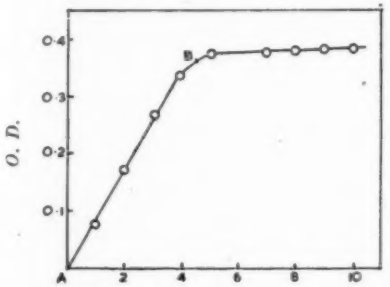


FIG. 1

A; 4.70 ppm Co, B; 1.88 ppm Co, C; 0.94 ppm Co.

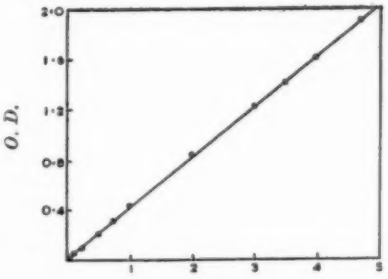
absorption due to the reagent at this wave length was negligible, and hence 485 mμ was chosen for all subsequent spectrophotometric studies of the red cobalt complex. A yellow complex formed between *p*H 1.5 and 6.5 did not show any maximum absorption at 400-700 mμ.

Minimum Amount of Oximidobenzotetronic Acid necessary for the Estimation of Cobalt.—For this study equimolar solutions of cobalt sulphate and oximidobenzotetronic acid were made. The optical densities at 485 mμ of a series of the above solutions containing oximidobenzotetronic acid and cobalt in the molar ratios of 1:1 to 10:1 were determined. The results are plotted in Fig. 2, where it is seen that the portion AB of the curve is a straight line up to the molar ratio of 4.5. For estimation of cobalt, the molar ratio of the reagent to cobalt was, however, maintained at 10 in the subsequent studies.



Variable component (c.c.).

FIG. 2



Cobalt (p.p.m.).

FIG. 3

Effect of pH on the Optical Density of Cobalt-oximidobenzotetronic Acid Complex.—The stock solution of the complex was 4.02×10^{-5} *M* with respect to cobalt. An aliquot (10 c.c.) of this solution was taken in a 25 c.c. measuring flask and the volume made to the mark using NaOH and HCl to bring the resultant solution to a *p*H value within 8.0 and 12.5. It was found that the absorption by the complex was maximum and unchanged above *p*H 10.0, as seen from Table I.

TABLE I

*p*H ..	8.0	8.7	9.0	9.4	10.0	10.8	11.3	12.0	12.5
O.D. ..	0.305	0.442	0.540	0.600	0.755	0.758	0.755	0.755	0.760

Between *p*H 7.0 and 8.0, the colour of the complex is yellowish red; below *p*H 7, it is yellow and a turbidity appears after about 10 minutes.

Stability of the Colour of the Complex.—The colour of the complex was found to be stable and no change in the optical density could be observed even after keeping the complex for one week. The effect of temperature on the optical density of the complex was also studied and no change in optical density was observed between 5° and 50°.

Lambert-Beer's Law.—The complex was found to obey Lambert-Beer's law between the concentration range of 0 to 4.7 p.p.m. at 485 mμ between *p*H 10.0 and 12.5. Under these conditions quantities as low as 0.02 p.p.m. of cobalt can be estimated. Fig. 3 shows the calibration curve.

Interference due to Foreign Ions.—The stock solution of the complex was $4.02 \times 10^{-5}M$ with respect to cobalt, having a mole ratio of the reagent to cobalt as 10. An aliqot (10 c.c.) of this solution was transferred to a 25 c.c. standard flask and mixed with a known amount of a foreign salt; the volume was made to 25 c.c. with water. The *p*H of the complex, however, was always maintained above 10.0. The concentration of the foreign salt in the complex was progressively increased till the optical density changed by 2% of the theoretical value. It was found that the anions borate, citrate, oxalate, phosphate, tartrate, fluoride, chloride, bromide, iodide, and sulphate did not interfere even if present in very large quantities. The concentrations of the following ions, which did not cause any interference, are shown in Table II.

TABLE II

Cations.	Taken as.	p. p. m. tolerated.
Aluminium	Aluminate	500
Beryllium	Beryllium sulphate (in presence of citrate ions)	800
Chromium	Chromate	250
Copper	Copper sulphate	36
Molybdenum	Ammonium molybdate	1,840
Manganese	Manganese sulphate (in presence of citrate ions)	800
Nickel	Nickel sulphate (in presence of citrate ions)	600
Tungsten	Sodium tungstate	2,400
Vanadium	Ammonium vanadate	240
Zinc	Zincate	552

Acetate ions did not interfere when present at a concentration of 800 p.p.m. for 1.8 p.p.m. of cobalt. Iron (II and III) interfered in the above estimation as the reagent formed a blue complex with iron.

Recommended Procedure for Cobalt Estimation

The given cobalt solution containing 0.02 to 4.0 p.p.m. of cobalt is treated with a fresh solution containing 10 times the reagent in minimum ethanol between the temperature range of 5° and 50° This results in the formation of a brownish red suspension. A 4% NaOH solution is then slowly added to the suspension till it dissolves completely with instantaneous formation of a deeply coloured red cobalt complex. The resultant solution is then diluted with water to a known volume and its optical density, determined at 485 mμ, is measured. The concentration of cobalt is then deduced from the standard calibration curve obtained under identical conditions.

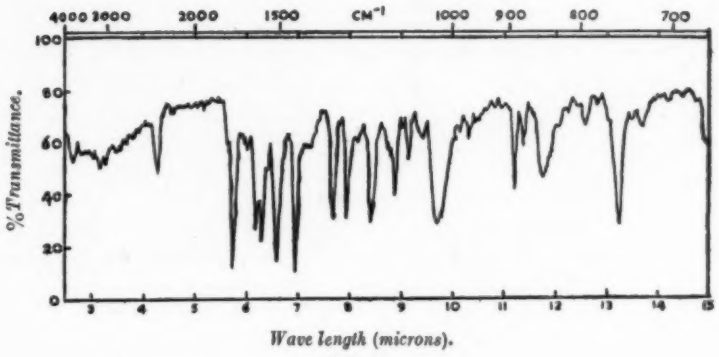
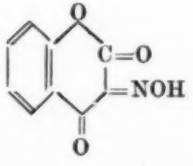


FIG. 4

Structure of Oximidobenzotetronic Acid

Anschütz (*loc. cit.*) gave structure (I) for oximidobenzotetronic acid. Taking chelation into account there are two possibilities (II and III) for the final structure. In order to decide between these two, a study of the infrared spectrum of the compound (Fig. 4) has been made. In potassium bromide pellet, the spectrum shows two absorption peaks at 1740 cm^{-1} and 1615 cm^{-1}, which could be attributed to carbonyl frequencies. This agrees very well with the requirements of formula (II), the ester carbonyl corresponding to 1740 cm^{-1} and the chelated carbonyl corresponding to 1615 cm^{-1}, although the alternative (III) could be expected to show the ester frequency much lower (1710 cm^{-1}) and the ketonic frequency much higher (1660 cm^{-1}).



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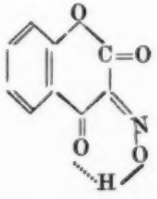

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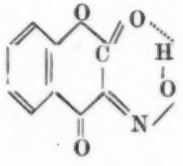

(III)

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SHORT NOTES

Synthesis of some 5-Arylazo-3-aryl-2-aryliminothiazolid-4-ones

Ravindra Pratap Rao

Introduction of azo group in several types of compounds has been found to considerably enhance their antibacterial activity. It was felt desirable therefore to study the effect of the introduction of azo group in the 3-aryl-2-aryliminothiazolid-4-ones on their fungicidal activity. With this aim in view the 5-arylazo derivatives of several 3-aryl-2-aryliminothiazolid-4-ones were prepared earlier by the present author (this *Journal*, 1958, **35**, 576) and Bhargava, Pantulu, and Rao (*ibid.*, 1957, **34**, 475). The present communication is in continuation of the earlier work. The results are reported in Table I.

TABLE I

Compound.	Colour.	Yield.	M.P.	Formula.	%Nitrogen. Found.	Calc.
5-Ph. azo-3-*m*-chloroPh-2-*m*-chloroPh-IT	Greyish brown	65%	135-37°	$C_{21}H_{14}ON_4Cl_2S$	12.73	12.69
5-Ph. azo-3-*p*-ethoxyPh.-2-*p*-ethoxyPh-IT	Dark greyish brown	67	106-108°	$C_{25}H_{24}O_3N_4S$	12.24	12.17
5-Ph. azo-3-β-naphthyl-2-β-naphthyl-IT	Greyish brown	70	170-72°	$C_{29}H_{20}ON_4S$	11.82	11.86
5-*p*-SulphonamidoPh.azo-3-*p*-ethoxyPh.-2-*p*-ethoxy-Ph-IT	Deep yellow	60	128-29°	$C_{25}H_{25}O_5N_5S_2$	13.05	12.98
5-*p*-SulphonamidoPh. azo-3-β-naphthyl-2-β-naphthyl-IT	Reddish brown	75	175-77°	$C_{29}H_{21}O_3N_5S_2$	12.65	12.70

Ph. = phenyl; IT = iminothiazolid-4-one.

The 3-aryl-2-aryliminothiazolid-4-ones were prepared according to the procedure of Markley and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 2137) and Rao (*loc. cit.*) and the 5-arylazo derivatives were obtained by the method described earlier (Rao, *loc. cit.*; Bhargava *et al.*, *loc. cit.*).

The author expresses his gratitude to Prof. R. C. Mehrotra and Dr. P. N. Bhargava for their kind interest during the progress of the work.

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Synthesis of Ethyl 3-Phthalimidoacetoacetate

J. K. Mehrotra and S. D. Verma

Ethyl 3-phthalimidoacetoacetate (IV) was first prepared by Gabriel (*Ber.*, 1909, **42**, 1244; 1913, **46**, 1706). To study the synthetic applicability of this compound, it was prepared by Gabriel's method in poor yield, attended with large amounts of unidentified byproducts among which two were isolated—one melting at 90—95° and the other at 116°. The identification of these compounds is still being carried out. The difficulty in the separation of these compounds led us to modify Gabriel's method. Thus ethyl 3-phthalimidoacetoacetate was prepared in 63% yield when, instead of sodium, ethoxymagnesium derivative of diethyl malonate (I) was used. Further, it had been found that ethyl 3-phthalimidoacetoacetate could be obtained in similar yields even without isolating the intermediate compound, diethyl phthalimidoacetomalonate (III).

$$\underset{\text{(I)}}{C_2H_5O.Mg.\ CH(COOC_2H_5)_2} + \underset{\text{(II)}}{C_6H_4(CO)_2N.\ CH_2CO.\ Cl} \longrightarrow$$

$$\underset{\text{(III)}}{C_6H_4(CO)_2N.\ CH_2CO.CH(COOC_2H_5)_2} \longrightarrow \underset{\text{(IV)}}{C_6H_4(CO)_2N.CH_2CO.CH_2COOC_2H_5}$$

Diethyl Phthalimidoacetomalonate.—In a one-liter, three-necked flask, containing 7 c.c. of dry ethanol and 1 c. c. of dry CCl_4, was placed 6.25 g. (0.258 g. atom) of clean Mg. A mixture of diethyl malonate (40g., 0.25*M*) and dry ethanol (20 c.c). was then added at such a rate that a vigorous reaction was maintained. When the evolution of hydrogen had subsided, dry ether (70 c.c.) was added and the mixture gently refluxed till all the Mg had dissolved. On removal of the solvent under diminished pressure the residue was dissolved in dry benzene (75 c.c.) and the latter removed as above. The residual syrup was dissolved in dry ether (75 c.c.) and phthalimidoacetyl chloride (56 g., 0.25 *M*), dissolved in dry ether (500 c.c.), was added to it with brisk stirring to maintain the vigour of the reaction. Finally the reaction mixture was refluxed for 1½ hours and then cooled. To the mixture 10% H_2SO_4 (100 c.c.) was added to decompose the MgCl-complex. The organic layer was separated and washed successively with H_2SO_4 (dil., 20 c.c.), water (2 × 20 c.c.), 5% $NaHCO_3$ (10 c.c.), and water (2 × 10 c.c.). Ether was removed when a slightly brown-coloured semisolid residue (86 g.) was obtained. The latter was rubbed with ethanol (10 c.c.) and chilled in ice. The precipitated *diethyl phthalimidoacetomalonate* was recrystallised from ethanol, m.p. 68° (lit. m.p. 68°), yield 55g. (Found: C, 58.61; H, 4.90; N, 4.30. Calc. for $C_{17}H_{17}O_7N$: C, 58.8; H, 4.9; N, 4.03%).

Ethyl 3-Phthalimidoacetoacetate.—The pure diethyl phthalimidoacetomalonate (55 g. or 86 g. of the crude semisolid residue obtained above) was steam distilled and then the

whole was extracted with benzene. The organic layer was filtered through cotton wool and the solvent removed. The residue was twice recrystallised from ethanol, when 43 g. of white needle-shaped crystals of the pure product, m.p. 110° (lit. m.p. 110°), was obtained. The yield amounted to 63% (Gabriel had not mentioned the yield), calculated on the basis of the acid chloride used. (Found: C, 60.98; H, 5.30; N, 4.98. Calc. for $C_{14}H_{13}O_5N$: C, 61.10; H, 4.73; N, 5.08%). This compound is soluble in hot ethanol, glacial acetic acid, ether, and benzene; its ethonolic solution developed a red colour with aq. $FeCl_3$, deepened on standing. *Semicarbazone* was obtained from ethanol as a white crystalline solid, m.p. 164°. (Found: C, 54.01; H, 4.80; N, 16.61. $C_{15}H_{16}O_5N$ requires C, 54.22; H, 4.82; N, 16.87%).

Pyralazone was obtained from ethanol as a white crystalline solid, m.p. 177°. (Found: C, 67.39; H, 4.46; N, 13.06. $C_{18}H_{15}O_3N_3$ requires C, 67.29; H, 4.73; N, 13.08%).

The authors wish to acknowledge their deep sense of gratitude to Dr. A. N. Dey for his keen interest in the work.

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3-Phenylthiazolid-2, 4-dione and some of its Derivatives

Ravindra Pratap Rao

3-Phenylthiazolid-2,4-dione was obtained by the method of Markley and Reid (*J. Amer. Chem. Soc.*, 1930, **52**, 2137) (cf. Liebermann and Voltzkow, *Ber.*, 1880, **13**, 276; Wheeler and Barnes, *J. Amer. Chem. Soc.*, 1900, **24**, 60, etc.).

Decomposition of this thiazolidione with caustic potash and dry distillation with sodalime, its reactions with benzaldehyde, and preparation of its acetoxymercuri derivative by an improved procedure (cf. Rout, this *Journal*, 1956, **33**, 690; Rout and Pujari, *J. Sci. Ind. Res.*, 1955, **14B**, 13) have been studied. Oxidation of the thiazolidione with potassium permanganate in acetic acid furnished the corresponding sulphone.

3-Phenylthiazolid-2,4-dione.—*S*-Diphenylthiourea (5 g.) and monochloroacetic acid (4 g.)were refluxed on a water bath in glacial acetic acid for about 2 hours. HCl (conc., 1.5 c.c.) was then added and refluxing continued for two and half hours more. The clear liquid was poured into water when a precipitate was obtained. It was washed with cold water to free it from excess acids, filtered, dried, and recrystallised from ethanol in the form of bushy rosettes of long, thin, faint yellow needles, yield 6g., m.p. 148°. (Found: N, 7.34. $C_9H_7O_2NS$ requires N, 7.25%).

Hydrolysis of 3-Phenyl-2-phenyliminothiazolid-4-one to 3-Phenylthiazolid-2,4-dione.—A mixture of 3-phenyl-2-phenyliminothiazolid-4-one (1.5 g.), ethanol (12 c.c.), and HCl (conc., 2 c.c.) was refluxed for 3½ hours. Ethanol was then distilled and water added; the precipitate which appeared was washed with cold water to remove acid and it was recrystallised from ethanol, yield 0.8 g., m.p. 148°. (Found: N, 7.29. $C_9H_7O_2NS$ requires N, 7.25%).

Decomposition with Potassium Hydroxide.—3-Phenylthiazolid-2,4-dione (1 g.) was heated with 40% KOH (30 c.c.) for 2½ hours. From the reaction mixture a liquid was isolated which was characterised as aniline by preparing its acetyl and azo-β-naphthol derivatives.

Dry Distillation with Sodalime.—The thiazolid-2, 4-dione (2 g.) was mixed with twice its weight of sodalime and subjected to dry distillation. The liquid thus obtained was identified to be aniline as in the above experiment.

5-Benzylidene-3-phenylthiazolid-2,4-dione.—A mixture of 3-phenylthiazolid-2,4-dione (1 g.), glacial acetic acid (10 c.c.), benzaldehyde (2 c.c.) and anhydrous sodium acetate (1.5 g.) was heated on an asbestos wire-gauze for 2 hrs. Water was added in excess and the mixture allowed to stand overnight. The precipitate was collected and recrystallised from acetic acid in light yellow crystals; yield 1.2g., m.p. 206°. (Found: N, 4.96; S, 11.42. $C_{16}H_{11}O_2NS$ requires N, 4.98; S, 11.37%).

3-*Acetoxymercuriphenylthiazolid*-2, 4-*dione*.—To 3-phenylthiazolid-2, 4-dione (1 g.), dissolved in ethanol-acetic acid, was added mercuric acetate (1.66 g.), dissolved in water acidified with acetic acid. The mixture was stirred vigorously and kept overnight. The precipitate was collected and washed repeatedly with hot water and dilute acetic acid. Finally it was washed several times with hot ethanol. The compound was isolated as a very light yellow powder, yield 1.22 g. (53% of theory), m.p. 246-48°. (Found: Hg, 44.49. $C_{11}H_9O_4NSHg$ requires Hg, 44.42%). The yield improved to 58% by directly refluxing for 15 minutes.

3-*Phenylthiazolid*-2, 4-*dione-sulphone*.—3-Phenylthiazolid-2,4-dione (1 g.) was dissolved in glacial acetic acid (20 c. c.) and treated slowly with potassium permanganate (1 g.) in water (25 c.c.) at 0°. After the reaction, excess of potassium permanganate was removed by treatment with sulphurous acid and the solution chilled with ice, when a precipitate was obtained. It was filtered, washed with ice-water, dried, and crystallised from ethanol in a light greyish powder; yield 0.98 g. (85% of theory), m.p. 250°. (Found: N, 6.19. $C_9H_7O_4NS$ requires N, 6.22%).

The author is thankful to Prof. R. C. Mehrotra, for his keen interest and to Dr. P. N. Bhargava, Reader in Chemistry, B. H. U., for his suggestions.

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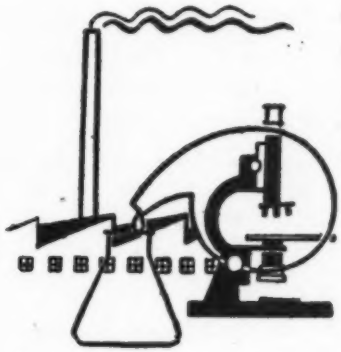

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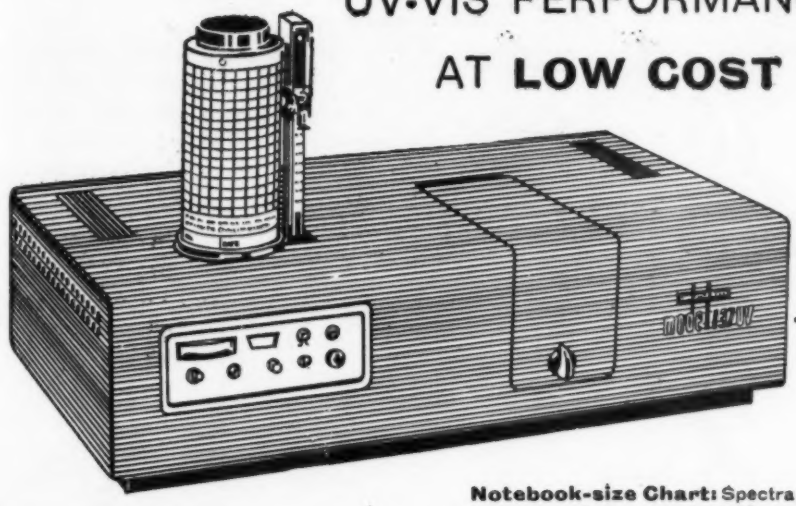

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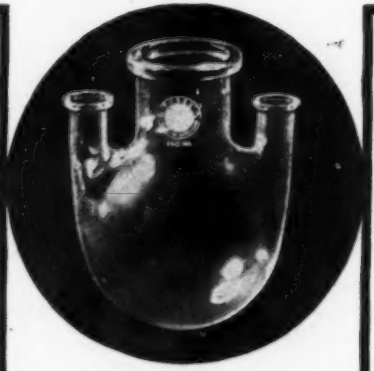

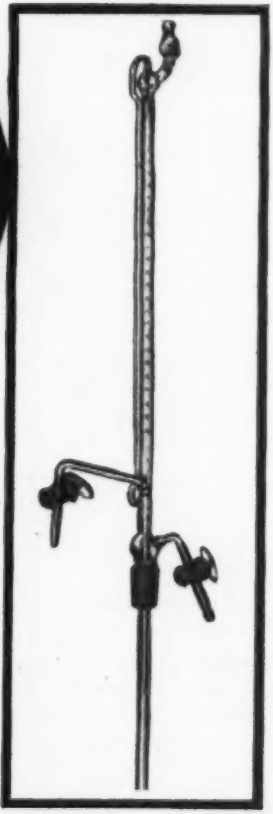

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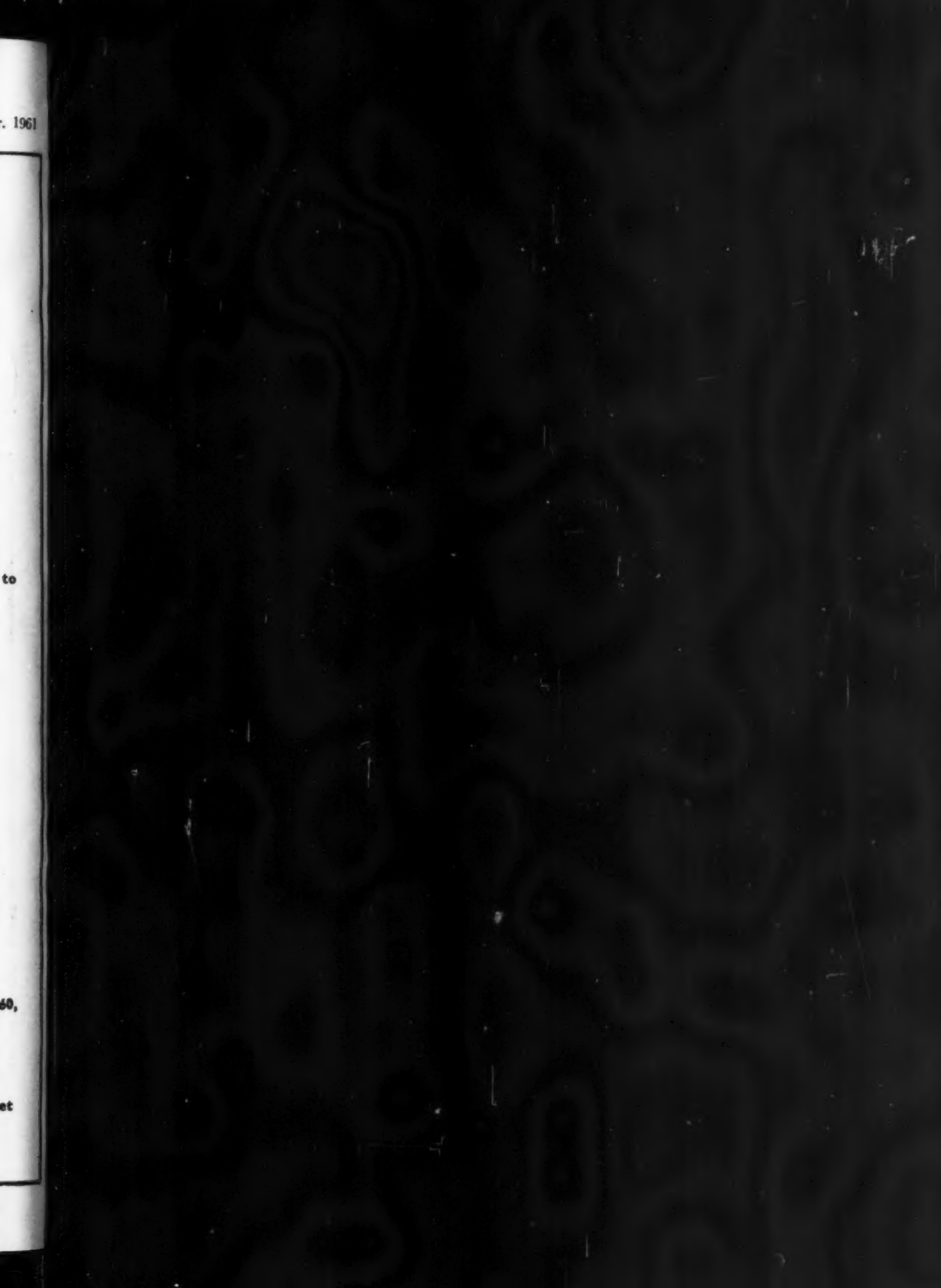

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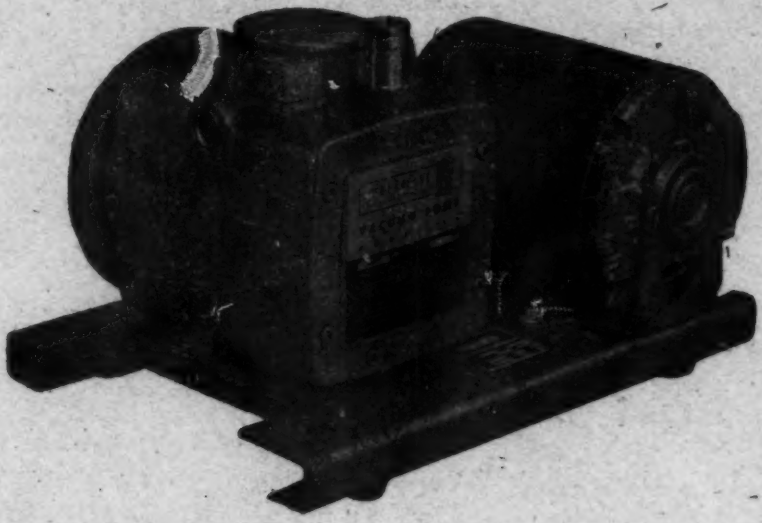

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